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ASSESSMENT OF THE POTENTIAL FOR TRANSPORT OF DIOXINS AND CODISPOSED MATERIALS TO GROUNDWATER

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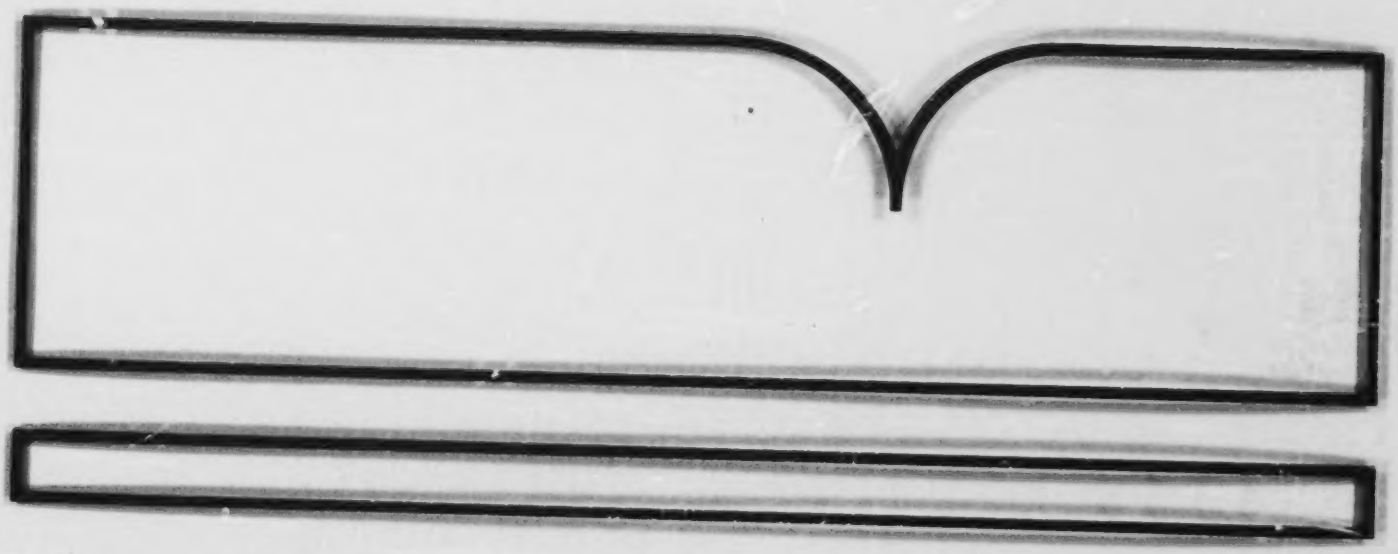

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ASSESSMENT OF THE POTENTIAL FOR TRANSPORT OF DIOXINS AND CODISPOSED MATERIALS TO GROUNDWATER

by

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16. ABSTRACT

Dioxins are very toxic contaminants and warrant study under a variety of experimental conditions. Studies were performed to evaluate the mobility of several of the dioxins in both soil columns as well as in batch experiments. The studies showed that the amount of chlorination did not necessarily control the partitioning of the dioxins, as expected, but also suggested that the structure or location where the Cl ion was attached to the benzene ring modified the hydrophobicity of the compound. Studies were performed with a variety of cosolvents which might mediate the movement of the Dioxin. The observed modification in mobility was consistent with existing theory for enhanced mobility with truly miscible solvents. Experimental data appears to show reversibility in the sorption process, but significantly limited by kinetics with 30 to 50 days required to release 50-90% of the contaminant.

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FOREWORD

EPA is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

This report presents experimental data on the partitioning (soil:water) of several chlorinated dibenzo-p-dioxins with soils and aquifer materials. The influence of truly miscible solvents, i.e., methanol, was found to follow existing theory. However, data suggest the effect of slightly soluble solvents such as chlorobenzene requires additional research.

Clinton W. Hall

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ABSTRACT

Parameters relevant to the sorptive transport of polychlorodibenzo-p-dioxins (PCDDs) through soils were evaluated in laboratory experiments involving batch shake testing and saturated-flow soil column techniques. The experiments were conducted by using water/methanol mixtures and four uncontaminated sorbents (two surface soils from Times Beach, MO and aquifer materials from Traverse City, MI and Lula, OK). Five ^{14}C-labeled PCDD congeners, including 2,3,7,8-tetra (T_4CDD), 1,2,3,4,7-penta, 1,2,3,4,7,8-hexa, 1,2,3,4,6,7,8-hepta, and octa, and three model codisposed materials (pentachlorophenol (PCP), chlorobenzene (CB) and diesel fuel), were utilized. The partition coefficient (K_D) for sorption of T_4CDD from water was found to be in good agreement with the water-phase K_D predicted by log-linear extrapolation according to the cosolvent theory by using K_D data generated for water/methanol mixtures. This observation validates the use of log-linear extrapolation to estimate water-phase K_D values for PCDDs using cosolvent data. K_D values for sorption of PCDDs by surface soils at volume fraction solvent (f_s) of 0.5-0.9 were reduced by a factor of up to 2.5 when PCP or CB were present. Reductions in K_D for PCDDs in the presence of PCP and CB increased with decreasing f_s. Additional research is necessary to determine whether further reductions in sorption occur at lower f_s to enable a better understanding of the influence of codisposed materials such as PCP and CB on the mobility of PCDDs under environmental conditions typified by low f_s (i.e., $f_s << 0.5$). Sorption K_D values for the aquifer materials were normalized on organic carbon content (f_{oc}) to yield values of K_{OC} which were in general agreement with K_{OC} values determined for the surface soils. This observation suggests that sorption by the organic matter content or the aquifer materials was sufficient to mask sorption to mineral surfaces. Desorption of PCDDs from the surface soils appeared to be reversible but was limited by kinetics, with roughly 50-90% of reversible-desorption equilibrium being attained within a contact period of 30-50 days.

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Dr. Marvin D. Piwoni assisted with the preparation of the work plan and preceded Dr. Carl G. Enfield as Project Officer for this project. The contributions of Drs. Piwoni and Enfield to the technical aspects of this project are gratefully acknowledged.

Dr. Jay C. Means contributed to the preparation of the proposal, work plan and quality assurance/quality control plan for this project.

SECTION 1

INTRODUCTION

Polychlorodibenzo-p-dioxins (PCDDs) are among the most toxic compounds known to man. For example, experimental studies of the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD or T_4CDD as referred to in this report) using guinea pigs have shown that the LD50 can range as low as 0.6 to 2.0 ug/kg of body weight (Esposito et al., 1980).

PCDDs as environmental contaminants have perhaps received most widespread national attention because they were present in waste oils which were used for dust control in Missouri (Exner et al., 1985). However, PCDD-contamination of soils and sediments in various locations throughout the U.S. (e.g., Love Canal) and in other countries (e.g., Seveso, Italy and Viet Nam) have been documented (Exner, 1987; Rappe, 1987). Concentrations of PCDDs in soil and sediment samples as high as 1600 ppb (Exner et al., 1985) to 100 ppm (Pereira et al., 1985) have been observed.

Until recently, it was believed that PCDDs were relatively immobile in soils because of their low water solubilities (e.g., Marple et al. (1986a) report an average water solubility for T_4CDD of 16 ng/L), and that there was little potential for PCDDs to be leached from contaminated soils. However, field observations have shown that PCDDs move faster through soils than would be expected based on their water solubilities (Ember, 1985). Numerous theories have been proposed to explain the "facilitated transport" of PCDDs and other highly hydrophobic organic contaminants, including the cosolvent theory proposed by Rao et al. (1985) which accounts for enhanced mobility in terms of the reduction in sorption by soils due to the presence of cosolvents.

Guiseppi-Elie (1987) and Yousefi (1986) have recently studied the effect of the presence of methanol, a model miscible

cosolvent, in water on the sorptive transport of PCDDs through surface soils. Guiseppi-Elie (1987) reported the results of experiments conducted by batch shake testing to evaluate the sorption of T_4CDD and four other PCDDs and the desorption of T_4CDD. Yousefi (1986) reported the results of experiments conducted by saturated-flow soil column techniques to evaluate sorption of T_4CDD and by batch techniques to evaluate the solubility of T_4CDD. These studies involved the development and application of experimental methodologies to evaluate sorption/desorption and solubilities of T_4CDD and other PCDDs in water/methanol mixtures, and are reviewed in greater detail in Section 4.

The research presented in this report was conducted to expand on the findings of Guiseppi-Elie (1987) and Yousefi (1986), and involved three basic objectives. The first objective was to determine the relative effect of the presence of codisposed materials on the sorptive transport of PCDDs through surface soils. Pentachlorophenol (PCP), chlorobenzene (CB) and diesel fuel were selected for use in these experiments as model solid and liquid materials of limited water solubility which are often codisposed at sites contaminated by PCDDs (ASTM, 1987; EPS, 1984; Hutzinger et al., 1985; Sheffield, 1985). Experiments were conducted to determine the effect of these materials on the solubility and sorption of PCDDs using water/methanol mixtures. The second objective was to evaluate the equilibrium sorption of PCDDs by aquifer materials. The third objective was to evaluate the kinetics of desorption of PCDDs from surface soils. Specific details regarding the rationale for and methodologies used in these experiments are presented in Section 6.

SECTION 2

CONCLUSIONS

The sorption and desorption of PCDDs by surface soils and the sorption of PCDDs by aquifer materials has been investigated by using batch shake testing and saturated-flow soil column techniques. Five C-14-labeled PCDDs, including T_4CDD, 1,2,3,4,7-penta (P_5CDD), 1,2,3,4,7,8-hexa (H_6CDD), 1,2,3,4,6,7,8-hepta (H_7CDD) and octa (O_8CDD), were utilized as solutes. Two surface soils from the Times Beach, MO area, with mass fraction organic carbon contents (f_{oc}) of 0.0066 (soil 91) and 0.077 (soil 96), and two aquifer materials with f_{oc} of 0.00017 (Traverse City) and 0.00021 (Lula), were utilized as sorbents. Experiments were conducted using water and water/methanol mixtures and three model codisposed materials (pentachlorophenol (PCP), chlorobenzene (CB) and diesel fuel).

Experiments to evaluate sorptive transport of PCDDs through surface soils included: (1) an investigation of the solubility behavior of the PCDDs and PCP in water/methanol mixtures; (2) an evaluation of the partition coefficient (K_D) for sorption of T_4CDD from water by soil 91; and (3) an investigation of the effect of the presence of PCP and CB on the sorption of PCDDs from water/methanol mixtures. Preliminary experiments were also conducted to assess the movement of diesel fuel through soil 91.

Sorption isotherm data were generated by batch techniques to evaluate the sorption of T_4CDD from water by soil 91. A contact period of 10 days, and a water prewash procedure which was used to remove nonseparable suspended particles (NSP) from the water phase, appeared to be adequate for evaluating an equilibrium K_D value which was not biased by the inadvertent sampling of NSP during liquid phase analysis. A linear sorption isotherm was obtained which indicated that K_D was 30,600 ($\log(K_D) = 4.49$). A value of $K_{m,oc}$ of 2.58×10^5 was determined by dividing this K_D value by f_{oc} and by the molar volume of water. This corresponds

to a value of $\log(K_{m,oc})$ of 5.41, which was in good agreement with the value of $\log(K_{m,oc})$ of 5.30 predicted by log-linear extrapolation of K_D data generated by Guiseppi-Elie (1987) for T_4CDD and soils 91 and 96 and water/methanol mixtures. This observation provides support for the applicability of the cosolvent theory to the sorption of PCDDs to soils from water/methanol mixtures over the entire range in f_s from 0.0-1.0, and provides justification for log-linear extrapolation using data generated for water/methanol mixtures to predict equilibrium water-phase K_D values for PCDDs and other highly hydrophobic organic contaminants.

The effect of the presence of PCP on the sorptive transport of PCDDs through soils was studied by using batch and column techniques, in which the liquid phase consisted of water/methanol mixtures ranging in f_s from 0.5-0.9 containing PCP at concentrations ranging from 1-10% of solubility. These experiments indicated that sorptive retention of PCDDs by soils was reduced by about a factor of 3 when PCP was present in the liquid phase relative to that observed in the absence of PCP.

The effect of the presence of CB on the sorptive transport of PCDDs through soils was studied by using column techniques, in which the liquid phase consisted of water/methanol mixtures ranging in f_s from 0.75-0.9 which contained CB at a concentration of 10 mL/L. These experiments indicated that sorptive retention of PCDDs by soils was reduced by a factor of 2 in the presence of CB at an f_s of 0.75 relative to that observed in the absence of CB.

Preliminary experiments were conducted to assess the feasibility of using batch and column techniques to study the sorptive transport of PCDDs through soils in the presence of diesel fuel. Batch techniques were found to be infeasible owing to the formation of multiple phases. Column experiments were conducted by using soil 91 in which liquid phase at f_s of 0.75 was passed through soil precoated with diesel fuel. These

experiments suggested that relatively stable water/methanol/diesel fuel emulsions were readily transported through the soil column. Further, although the soil column had been apparently flushed of diesel fuel at a high relative velocity, it was observed that the column had a residual capacity to retain significant amounts of diesel fuel which was released from the column as a stable emulsion at low liquid-phase flow rates.

Experiments to evaluate the sorption of PCDDs by aquifer materials included an assessment of sorption kinetics and equilibrium K_Ds. The results of these experiments suggested that a two-day contact period was sufficient to achieve sorption equilibrium for all PCDDs studied. Sorption isotherm data were generally linear, and equilibrium K_Ds, when converted to K_m, were log-linearly related to f_s in accord with the cosolvent theory. When K_m values were normalized on f_{oc} of the aquifer material, the resulting $K_{m,oc}$ values were in general agreement with $K_{m,oc}$ values determined for surface soils from the Times Beach, MO area. It is suspected that the agreement between aquifer material and surface soil sorption for PCDDs suggests that sorption to organic carbon is sufficient to mask sorption to mineral surfaces.

Experiments to evaluate the desorption of PCDDs from surface soil were conducted by batch techniques, in which PCDDs were previously sorbed by soil for thirty days prior to the initiation of the desorption experiments. The results of these experiments suggested that desorption appeared to be generally reversible but was limited by kinetics, with roughly 50-90% of reversible-desorption equilibrium being attained within a 30-day contact period.

SECTION 3

RECOMMENDATIONS

The research presented in this report has contributed significantly to knowledge regarding the sorptive transport of PCDDs and organic contaminants of similarly-high hydrophobicity through soils. Additional research in six areas is recommended to further improve knowledge of the transport of PCDDs and related contaminants through soils:

1. Sorption of PCDFs. A substantial data base has now been compiled regarding the sorption of PCDDs by soils. However, no data have been reported on the sorptive partitioning of polychlorodibenzofurans (PCDFs). High-purity standards of these contaminants are now available in radiolabeled form, and it is suggested that issues relevant to sorptive partitioning be investigated using several PCDF congeners.

2. Sorption from Water/Methanol Mixtures. The sorption of PCDDs as a function of volume fraction cosolvent (f_s) for water-miscible cosolvents is generally well understood. However, further research is necessary to better understand solubility and sorption behavior at low f_s (e.g., for f_s below 0.05-0.1). This work should be conducted using PCDDs and PCDFs as well as slightly less hydrophobic contaminants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Research should also be initiated to evaluate the cosolvent effects attributed to ethylene glycol, a water-miscible solvent which is relevant to the manufacturing process of PCP and thus relevant to waste sites contaminated by PCDDs.

3. Sorption in the Presence of Codisposed Materials. Additional research is needed to better understand the sorption of PCDDs and related contaminants in the presence of codisposed materials. Three groups of codisposed materials can be identified. The first group is slightly soluble solvents; much

is known regarding the sorption of hydrophobic contaminants in the presence of miscible cosolvents such as methanol and acetone, but little is known regarding the effect of immiscible solvents such as methylene chloride, benzene, and aniline. The second group is slightly soluble solids; the effect of the presence of 2,4,5-trichlorophenol and terpenes, as well as PCP, at low f_s should be evaluated. The third group is oil/carrier liquids. There appears to be a significant need to further understand the movement of oil through soils, and the manner in which oil movement affects the sorptive transport of PCDDs and codisposed materials. Research should thus be conducted to evaluate the sorptive transport of oils, oils and PCP, and oils, PCP and terpenes, as well as the sorptive transport of PCDDs in the presence of these materials. This research should focus on evaluating the relative contributions to transport attributed to dissolved oil constituents versus oil droplets and oil/water emulsions, including water-phase sorption-desorption, dislodging of intrapped droplets, and potential for emulsion formation.

4. Sorption of PCDDs in the presence of colloids. Much is known regarding the sorptive transport of moderately hydrophobic organic contaminants in the presence of colloidal organic matter, and this work suggests that colloids can substantially increase the mobility of organic contaminants through soils. Additional work is necessary to extend this research to include highly hydrophobic organics such as PCDDs.

5. Sorption of PCDDs by aquifer materials. Additional research is needed to evaluate the relative mineral contributions to sorptive transport of PCDDs and similar organics through low-f_{oc} aquifer materials. This research should focus on organic contaminants with relatively high hydrophobicity, such as PAHs and PCBs as well as PCDDs, and on a variety of sorbents to enable a better fundamental understanding of the relative effects of K_{ow}, mineral surface area and f_{oc} on sorption to low-f_{oc} sorbents.

6. Desorption of PCDDs. Desorption of PCDDs from soils at low f_s and in the presence of codisposed materials such as oil should be investigated. This research should include development of a model which incorporates desorption kinetics to enable better prediction of the movement of PCDDs through soils under real-world conditions.

SECTION 4

BACKGROUND

CONTAMINANT TRANSPORT THROUGH SOILS

The transport of contaminants through soils can be generally described in terms of the processes of advection, dispersion, sorption and degradation (Roberts et al., 1982). For hydrophobic organic contaminants such as PCDDs which are essentially non-reactive and have low water solubilities, the dispersion and degradation terms are generally insignificant and contaminant transport can be described in terms of advection and sorption. Under these conditions, the transport of a solute in one-dimensional, single-phase flow in a saturated, consolidated, homogeneous medium can be described by equation (1) (Roberts et al., 1982):

$$-V(\partial C/\partial x) - (\rho_B/\varepsilon)(\partial S/\partial t) = \partial C/\partial t \qquad (1)$$

where V = average fluid velocity (m/s), C = liquid-phase concentration of the solute (g/m^3), x = distance in the direction of flow (m), ρ_B = bulk density of the soil (g/m^3), ε = soil void fraction (dimensionless), S = mass of solute sorbed per unit of dry mass of soil (g/g) and t = time (s).

The sorption of hydrophobic organic contaminants to soils from water has been extensively studied and is generally well understood (Karickhoff, 1984). Under equilibrium conditions and for relatively dilute solute concentrations, solute liquid-phase and soil-phase concentrations are related by:

$$S_e = K_D C_e \qquad (2)$$

where K_D is the equilibrium sorption partition coefficient (m^3/g) and the subscript e is used to denote equilibrium. For a given

soil-solute system, K_D has been found to be a function primarily of the mass fraction of organic carbon (f_{oc}) of the soil and of the water solubility (S_w) or octanol-water partition coefficient (K_{ow}) of the solute. The value of K_D has been found to be linearly related to f_{oc}:

$$K_D = K_{oc}f_{oc} \tag{3}$$

which defines the proportionality constant K_{oc}, the partition coefficient normalized on the organic carbon content of the soil. Numerous relationships have been reported which show that values of $\log(K_{oc})$ are linearly related to $\log(S_w)$ or $\log(K_{ow})$. For example, Lyman et al. (1982) present the following relationships derived from the data of a wide variety of compounds, mostly pesticides:

$$\log(K_{oc}) = -0.55\log(S_w) + 3.64 \tag{4}$$

where S_w is expressed in units of mg/L, and:

$$\log(K_{oc}) = 0.544\log(K_{ow}) + 1.377 \tag{5}$$

If the assumption is made that local sorption equilibrium is maintained (i.e., that the sorption equilibration rate is rapid relative to the liquid-phase velocity), then equation (1) becomes:

$$-V(\partial C/\partial x) = [1 + (\rho_B K_D/\varepsilon)](\partial C/\partial t) \tag{6}$$

The term $[1 + (\rho_B K_D/\varepsilon)]$ in equation (6) is known as the solute retardation factor, the reciprocal of which is known as the relative velocity of the solute concentration front (V_r):

$$V_r = 1/[1 + (\rho_B K_D/\varepsilon)] \tag{7}$$

where $V_r = V_c/V$ and V_c = average velocity of the concentration front of the solute (m/s). Equation (7) presents a simplified though useful model which indicates that, for a given soil, solute transport is dependent upon physical characteristics of the soil and on the K_D of the solute.

CONTAMINANT TRANSPORT IN THE PRESENCE OF COSOLVENTS

Based on the simple transport model of equation (7), transport of PCDDs to groundwater as a result of leaching from contaminated soils is expected to be quite low. This expectation is based on the low water solubility (S_w) (e.g., Marple et al. (1986a) report an average S_w for T_4CDD of 16 ng/L) and high octanol-water partition coefficient (K_{ow}) (e.g., Marple et al. (1986b) report $\log(K_{ow})$ for T_4CDD of 6.64) of PCDDs. These properties suggest that PCDDs would have high values of K_D (using equations (4) and (5), $\log(K_{oc})$ for T_4CDD is predicted to be 5.1-6.4) and would thus be expected to be sorbed strongly by soils. Laboratory experiments to evaluate the movement of 1,3,6,8-TCDD through soils by water-phase leaching have confirmed the low mobility of PCDDs (Helling et al., 1973). However, there have been reports based on the analyses of field samples that T_4CDD and other PCDDs move more rapidly through soils than would be expected based on equation (7) (Ember, 1985). This "facilitated transport" has been explained in terms of numerous potential factors including enhanced solubility due to the presence of organic cosolvents (Rao et al., 1985; Nkedi-Kizza et al., 1985; Fu and Luthy, 1986b) and/or other codisposed organic materials in the liquid phase.

Rao et al. (1985) developed the cosolvent theory to incorporate the effect of the presence of a miscible organic cosolvent on K_D. The theory predicts a log-linear relationship between the mole-based equilibrium sorption partition coefficient (K_m) and the volume fraction cosolvent (f_s):

$$\log(K_{m,i}) = \log(K_{m,w}) - \alpha\sigma_s f_s \quad (8)$$

where $K_{m,i}$ and $K_{m,w}$ are mole-based partition coefficients (mol/g) for water/solvent mixture i and solvent-free water, respectively. Values of $K_{m,i}$ are related to $K_{D,i}$ by:

$$K_{m,i} = K_{D,i}/V_i \quad (9)$$

where V_i is the molar volume of the liquid phase (mL/mol). The σ_s term in equation (8) reflects solute-liquid interactions in that it is the slope of the log-linear relationship between mole fraction solubility and f_s (Fu and Luthy, 1986a):

$$\log(X_i) = \log(X_w) + \sigma_s f_s \quad (10)$$

where X_w and X_i are mole-fraction solubilities of the solute in water and water/solvent mixture i, respectively. The α term in equation (8) is related to solute-soil and solvent-soil interactions via liquid and organic carbon phase activity coefficients (Rao et al., 1985; Fu and Luthy, 1986a). Equation (8) has been found to describe the sorption of several hydrophobic organic contaminants to soils from water/methanol mixtures (Nkedi-Kizza et al., 1985; Fu and Luthy, 1986b).

The cosolvent theory is important for two reasons. First, the theory enables prediction of sorption of an organic solute from a specified mixture of water and miscible organic solvent. This has implications on understanding fate and transport of organic contaminants in real-world, complex waste streams such as industrial wastes and landfill leachates. Second, the theory can be utilized to estimate K_D for sorption from aqueous solution by log-linear extrapolation of $K_{D,i}$ data generated at higher f_s. This is particularly significant for highly hydrophobic compounds such as PCDDs because direct experimental determinations of sorption from water are extremely difficult to make.

TRANSPORT OF PCDDS IN WATER/METHANOL MIXTURES

Guiseppi-Elie (1987) studied the sorption of five chlorodibenzo-p-dioxin (CDD) congeners, including T_4CDD, 1,2,3,4,7-pentaCDD (P_5CDD), 1,2,3,4,7,8-hexaCDD (H_6CDD), 1,2,3,4,6,7,8-heptaCDD (H_7CDD) and octaCDD (O_8CDD), to surface soils from water/methanol mixtures. This study utilized batch shake testing, and was limited to studying sorption of the noted PCDDs for $0.5 \leq f_s \leq 0.75$. Sorption at lower f_s could not be readily evaluated because of suspected interferences in determination of C_e due to the presence of nonseparable soil particles, while sorption at higher f_s was generally too weak to measure. The main conclusions from this study were: (1) the rate of sorption of PCDDs to surface soils was positively related to f_s and negatively related to PCDD molecular weight, and was also sensitive to soil characteristics (e.g., composition and perhaps amount of soil organic matter); (2) contact periods of 30-45 days were necessary to achieve sorption equilibrium for the soil which had the highest f_{oc}; (3) equilibrium K_Ds for the PCDDs, converted to K_m, were log-linearly related to f_s according to equation (8); and (4) preliminary studies of the desorption of T_4CDD suggested that desorption was at least partially reversible and was limited by slow desorption kinetics.

The observation of Guiseppi-Elie (1987) that equation (8) applied to the sorption of PCDDs to soils from water/methanol mixtures enabled estimation of water-phase K_D values for the PCDDs by log-linear extrapolation using cosolvent data. Direct experimental determination of water-phase K_D for T_4CDD was attempted to verify that the log-linear relationship extended to f_s of 0.0 for highly hydrophobic compounds such as PCDDs. However, these experiments were not successful for numerous reasons, including the potential presence of suspended material in the liquid phase which interferred with determination of C_e and the relatively high detection limits for the radiolabeled T_4CDD in comparison to solubility. It was suggested that

modified batch shake testing techniques be used to evaluate K_D for at least one PCDD to verify the cosolvent theory at low f_s.

Yousefi (1986) utilized saturated-flow soil column techniques to study the sorption of T_4CDD to soils from water/methanol mixtures and other solvents and developed a technique to evaluate the solubility of T_4CDD in water/methanol mixtures. Both sorption and solubility experiments were limited to relatively high f_s. The soil column experiments utilized pulse and step inputs of T_4CDD. Apparent or observed K_Ds (referred to as K_{obs}) were estimated by the retention of T_4CDD by the soil column relative to the liquid flow by using equation (7). These experiments indicated that column techniques could be utilized for estimating sorption K_Ds for $K_D \leq 10$ (i.e., for $f_s > 0.75$. Comparison of a limited set of K_D values generated by batch techniques (Guiseppi-Elie, 1987) to those estimated from column experiments suggested that K_{obs} values underestimated actual K_D by roughly 30%.

Yousefi (1986) documented the utility of column techniques for estimating K_D, and noted that column techniques offer several advantages over batch techniques for studying the sorption of PCDDs. One important advantage noted for using column experiments was that substantially less solute was needed to obtain an estimate of K_D than was needed in batch studies to generate sorption isotherm data. This has implications on safety concerns and on experimental costs associated with studies involving radiolabeled PCDDs, which are both highly toxic and expensive. Column techniques were also recognized as being useful for studying the relative effect of liquid-phase composition on K_D.

The solubility experiments reported by Yousefi (1986) for T_4CDD were performed to generate data to enable evaluation of σ_s in equation (10). These experiments were conducted by batch techniques using 1-mL microvials. Various techniques were tested to reduce the likelihood of inadvertent sampling of

microparticulates in the liquid phase. The experimentally-determined solubility of T_4CDD in methanol using this technique was in good agreement with published values.

SECTION 5

MATERIALS AND METHODS

MATERIALS

Solutes

All PCDDs used in experiments described in this report were radiolabeled with C-14. Labeled 2,3,7,8-TCDD (T_4CDD) with specific activities of 33.24 and 117.54 mCi/mmol was obtained from Cambridge Isotope Laboratories, Inc. (Cambridge, MA). The former was used in experiments involving cosolvent mixtures, while the latter was used in the water-phase sorption experiments. Labeled 1,2,3,4,7-PCDD (P_5CDD), 1,2,3,4,7,8-HCDD (H_6CDD), 1,2,3,4,6,7,8-HCDD (H_7CDD) and 1,2,3,4,5,6,7,8-OCDD (O_8CDD) with specific activities of 24.16 mCi/mmol, 24.16 mCi/mmol, 24.2 mCi/mmol and 20.58 mCi/mmol, respectively, were obtained from Pathfinder Laboratories Inc. (St. Louis, MO). These materials had chemical and radiochemical purities of $\geq$ 98% and >99.99%, respectively, and were used as received without further purification. Individual stock solutions of the radiolabeled PCDDs were prepared by dissolving them in methanol with the exception of O_8CDD, which was dissolved in methylene chloride. Stock solutions were stored in amber-glass bottles and were refrigerated when not in use.

Other radiolabeled compounds which were used included pentachlorophenol (PCP), methanol and water. C-14 labeled PCP with specific activity of 13.5 mCi/mmol was obtained from Pathfinder. The chemical and radiochemical purities of the PCP were 98.3% and 100.0%, respectively. C-14 labeled methanol with specific activity of 7.0 mCi/mmol and chemical and radiochemical purities of >99% was obtained from New England Nuclear (Boston, MA). H-3 labeled water with specific activity of 1.6 mCi/mmol was provided by Dr. Jay C. Means of the Chesapeake Biological Laboratory. These materials were used as received without

further purification.

Unlabeled PCP with chemical purity in excess of 99% was obtained from Fluka Chemical (Ronkonkoma, NY). Diesel fuel was obtained from a local Chevron service station. These materials were used as received without further purification.

Soils and Aquifer Materials

Two surface soils from the Times Beach, MO area and two aquifer materials were used in experiments described in this report.

The soils from Times Beach were those used in previous investigations of the sorption of PCDDs to soils (Guiseppi-Elie, 1987). These soils were air dried and sieved through 0.3 mm standard sieves, and were characterized for pH, cation exchange capacity (CEC), organic matter content, organic carbon, organic nitrogen and texture. U.S. EPA location and site identification numbers and characterization data for these soils are listed in Table 1. The soils are referred to in this report as soil 91 (the low-organic carbon soil) and soil 96 (the high-organic carbon soil).

Lula and Traverse City aquifer materials were provided by the EPA Project Officer and were used as received. Identification and characterization data for these samples were furnished by the EPA Project Officer and are listed in Table 2.

Solvents

All solvents (methanol and methylene chloride) used in experiments described in this report were pesticide grade obtained from Fisher Scientific or VWR Scientific, and were used as received without further purification. Water was generated by using a water treatment system from Hydro (Rockville, MD) consisting of a reverse osmosis unit, activated carbon bed and a

Table 1. Identification and Characterization Data for Surface Soils from the Times Beach, MO Area.

Soil Number		91	96
EPA Sampling Location		Sontag Road	Piazza Road
EPA Site Number		04114B	06126B
pH		6.8	5.8
CEC, meq/100 g		5.4	15.3
Organic Carbon, %		0.66	7.7
Texture:	Sand, %	44	38
	Silt, %	42	40
	Clay, %	14	22

Table 2. Identification and Characterization Data for Traverse City and Lula Aquifer Materials.

Aquifer Material	Traverse City	Lula
Sample Location	1A-4, 5, 6 and 7	C1, Split I/1
Organic Carbon, %	0.017	0.021
Surface Area, m^2/g		11 $\pm$ 1.2
CEC, meq/100 g		2.5
Clay, %		14

pair of mixed bed deionizers. Water from this system was dosed with 0.01% by weight NaN_3 as a biocide and the ionic strength was adjusted to 0.01 M using $CaCl_2$. The pH of the water was adjusted to 7.0 using NaOH.

Scintillation Cocktail

Insta-gel liquid scintillation cocktail obtained from United Technologies was used for all radioisotope analyses.

ANALYSES

Liquid Scintillation Counting

Analytical determinations were made by liquid scintillation counting (LSC) using a Model 1219 Rackbeta liquid scintillation counter obtained from LKB Instruments, Inc. (Gaithersburg, MD).

Liquid-phase solute concentrations (C or C_e) were determined by sampling three aliquots of 1-3 mL of liquid phase and adding the sample to 10-mL of Insta-gel cocktail in 20-mL glass counting vials. Automatic quench correction using an external standard and fluorescence correction were employed on all samples.

Soil-phase solute concentrations (S or S_e) were determined primarily by difference (i.e., by dividing the difference between total solute added to the tube and the total solute in the liquid phase by the mass of soil or aquifer material added to the tube). Direct determination of soil-phase solute concentrations was made in screening experiments to confirm mass balances. In this case, the total soil sample (0.3-1 g) was analyzed either by adding it directly to 10-mL of counting cocktail or by extracting it using 3 25-mL volumes of methylene chloride, reducing the extract volume to 3-mL by evaporation into nitrogen, and adding the extract to 10-mL of cocktail.

Turbidity

Turbidity measurments of column effluent from diesel fuel experiments were made using a Model 2100A Hach turbidimeter (Loveland, CO). Standards consisting of diesel fuel in a liquid phase at f_s of 0.75 were prepared by adding 15, 100 and 1,000 uL of diesel fuel to 10-mL of liquid phase. Samples were shaken manually for 5 minutes, and were then analyzed for turbidity. The turbidity of these samples was found to be 100, 420 and 900 NTU, respectively. These results are shown in Figure 1, which was used as a calibration curve (for purposes of estimation only) to determine relative diesel fuel composition in experiments in which emulsions containing diesel fuel were encountered.

DATA MANIPULATION

Isotherm data were evaluated by linear regression to determine best-fit parameters for equation (2) and statistical parameters according to techniques presented by Gillingham and Heien (1971) and McCuen (1985). The best-fit estimate of K_D, the coefficient of determination (r^2) and the standard error of the estimate (s) were calculated from:

$$K_D = \Sigma C_{e,i} S_{e,i} / \Sigma C_{e,i}^2 \quad (11)$$

$$r^2 = K_D \Sigma C_{e,i} S_{e,i} / \Sigma S_{e,i}^2 \quad (12)$$

$$s = [\{ \Sigma (S_{e,i} - K_D C_{e,i})^2 \}/(n - 1)]^{0.5} \quad (13)$$

where n = the number of isotherm data points included in the regression analysis.

Values of K_{obs} were determined from the effluent concentration profiles obtained from saturated-flow soil column experiments. K_{obs} is the value of K_D calculated by using equation (7) and a value for V_r equal to the ratio of sorbing

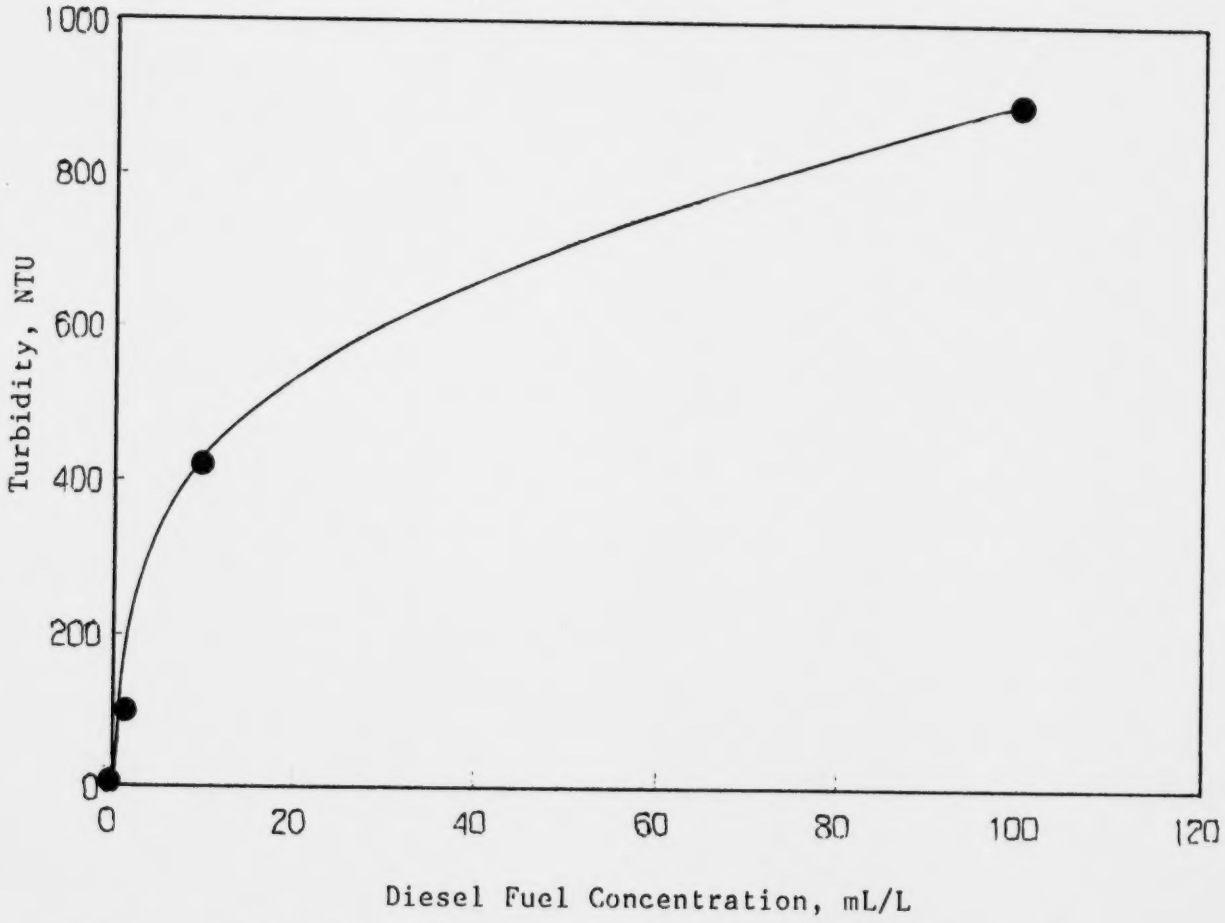

Figure 1. Calibration Curve Relating Diesel Fuel Concentration and Turbidity.

solute to nonsorbing solute retention time as determined by the center-of-mass of the respective effluent peaks.

Least-squares regression analysis was used to determine the best-fit estimates of the slope (m) and intercept (b) for equations (8) and (10). The values of m and b and the regression statistics were determined by using standard techniques (McCuen, 1985).

Desorption data were regressed according to exponential and power-curve models:

$$K_{des} - K_D = a_1 e^{-b_1 t} \tag{14}$$

$$K_{des} - K_D = a_2 t^{b_2} \tag{15}$$

In equations (14) and (15), t is the length of the desorption contact period (days), K_{des} is the observed partition ratio (S/C) following a desorption contact period t (mL/g), K_D is the partition ratio characterizing the sorption state attained prior to initiating the desorption experiment (mL/g), and a_i and b_i are empirical constants evaluated by regression analysis.

SECTION 6

EXPERIMENTAL PROCEDURES

SOLUBILITY DETERMINATIONS

The batch technique developed by Yousefi (1986) to evaluate T_4CDD solubility in water/methanol mixtures was used to evaluate the solubilities of the other PCDDs. These experiments were conducted by using 1-mL glass microvials with an internal conical shape. PCDD crystals were precoated onto the inner wall near the bottom of the microvial by delivering 100-uL of a working solution containing the PCDD and evaporating the solvent into a gentle stream of nitrogen. One mL of liquid phase was then added to the precoated microvial, the vials were capped and covered with aluminum foil, and were placed on a shaking table. The vials were then shaken daily for 15 minutes for contact periods up to 28 days. Each experiment was prepared in triplicate, and following the specified contact period the liquid phase in each of the triplicate vials was sampled by taking three 100-uL aliquots for triplicate analysis by LSC.

BATCH SHAKE TESTING

The batch shake testing technique which was used to generate data presented in this report was similar to that employed by Guiseppi-Elie (1987) to evaluate sorption and desorption of PCDDs to/from soils. One procedure was utilized for systems involving water/methanol mixtures, and a second procedure was utilized to evaluate sorption from water.

Experiments Involving Water/Methanol Mixtures

Batch experiments involving water/methanol mixtures were conducted using 15-mL conical glass centrifuge tubes fitted with aluminum foil- and Teflon-lined screw caps.

Tubes were dosed by direct addition of soil or aquifer material, liquid phase and solute. Soil or aquifer doses added to the tubes typically ranged from 0.2-1.0 g, and were selected where possible to result in 20-80% of total solute added to each tube being sorbed (McCall et al., 1981). Solute doses were delivered by direct dosing of 5-100 uL of stock solution. Dosing volumes were selected so as to result in liquid phase concentrations ranging from analytical detection limits (50 dpm) to the estimated upper limit of 50% of solubility below which sorption isotherms were expected to be linear (Karickhoff, 1984). A liquid-phase volume of 12-mL was added to the tubes except for experiments involving PCP as solute in which case the tubes were filled completely with liquid phase.

Liquid phase solutions at varying f_s with and without unlabeled PCP or CB, were prepared and stored in 1-L amber glass bottles fitted with Teflon lined screw caps. Liquid phases containing either PCP or CB were used immediately after preparation to minimize volatile losses of the solute.

Experiments conducted to evaluate the sorption of PCDDs in the presence of PCP and CB were performed by using relatively high concentrations of PCP and CB to identify gross effects that these materials might have on sorption. However, solution concentrations well below saturation were utilized so as to avoid numerous potential problems (e.g., crystallization effects). Consequently, PCP and CB concentrations ranging from roughly 1-10% of solubility were generally used in sorption experiments.

After the tubes were dosed, they were placed horizontally on a shaking table and were shaken for fifteen minutes every hour. Contact periods ranged from 2 hr to 30 days and varied according to the type of experiment (kinetic versus equilibrium) and the soil-solute-liquid phase system under study. Following contacting, tubes were removed from the shaking table and centrifuged at 3,000 rpm (2,000xg) for 10 minutes by using a Model GPR temperature-controlled centrifuge equipped with a Model

GH-3.7 four-place horizontal rotor obtained from Beckman (Columbia, MD). This extent of centrifugation was found to achieve adequate separation of liquid and solid phases so that liquid phase concentration determinations were not influenced by inadvertent sampling of suspended soil particles.

Water-Phase Experiments

Two batch procedures were utilized to generate isotherm data for the sorption of T_4CDD from water by soil 91. Both sets of experiments were conducted by using 50-mL round bottom glass centrifuge tubes fitted with Teflon-lined screw caps. Soil and water doses to the tubes were approximately 50 mg and 40 mL, respectively. Each isotherm consisted of duplicate tubes which were dosed with one of three T_4CDD dosages.

In the first procedure, tubes were dosed and capped, and the contents were contacted for 48 hours on a shaking table. Tubes were then centrifuged at 3,000 rpm for 10 minutes, and the water-phase was removed for analysis as described below.

The second procedure was designed to investigate the effects of contact period and soil-water separation procedure on the sorption isotherm data. A prewash of the soil with water prior to dosing the tubes with T_4CDD was performed to assess the extent to which the water-phase evaluations were influenced by the presence of macromolecules and/or microparticulates which were not separated during centrifugation. These experiments involved a prewash procedure similar to that of Gschwend and Wu (1985) which consisted of (1) contacting the soil and water for 48 hours; (2) separating soil and water by centrifuging at 1800 rpm for 30 minutes; and (3) withdrawal and replacement of the supernate with fresh water. This prewash procedure was performed five times before tubes were dosed with T_4CDD. Tubes were then dosed with T_4CDD and the contents were contacted for ten days, after which the tubes were centrifuged at 3,000 rpm for 60 minutes. The supernate water phase was then withdrawn for analysis.

The water-phase analysis for both procedures involved withdrawing 30 mL of supernate using a 15-mL class A Kimax pipet. The water sample was delivered to a 125-mL glass separatory funnel, and was extracted four times with 5 mL of methylene chloride by a gentle swirling action. Each 5-mL volume of extract was drained into a counting vial, and the total 20-mL volume was reduced to about 5-mL by evaporating the methylene chloride into a gentle stream of nitrogen gas. Ten-mL of counting cocktail was added to the vials, and the mixture was analyzed by LSC.

An experiment was conducted to determine the extraction efficiency and percent recovery of T_4CDD by the methods described above. This experiment involved extraction and analysis of 30.0-mL of water which was dosed with 10-uL of the T_4CDD working solution, as well as analysis of a 10-uL sample of the T_4CDD working solution which was delivered directly to a counting vial. The results of this experiment are shown in Table 3, and indicated an extraction efficiency of 92-100%. Based on the results of this experiment, extraction efficiency corrections were not applied to the measured water-phase concentrations.

An experiment was also conducted to evaluate the amount of T_4CDD which was associated with the tube walls and Teflon cap liners for each of the tubes involved in the isotherm experiment conducted using the second procedure. Following the sampling of the 30-mL volume of water for analysis, the remaining water and soil phases were withdrawn from the tubes by using a Pasteur pipet, and the emptied tubes were sealed and rinsed with three 5-mL volumes of methanol followed by one rinse with 5-mL of methylene chloride. The rinses for each tube were delivered to a counting vial and the volume was reduced to 5 mL by evaporation of the mixture into a gentle stream of nitrogen gas. Counting cocktail was added to the extract, and the sample was analyzed by LSC. The results of this experiment are summarized in Table 4, and indicated that 3.5 ± 0.8 % of the T_4CDD dosed to the tubes was associated with the tube walls and/or cap liner. No attempt

Table 3. Results of Extraction Efficiency Experiments for Recovery of T_4CDD from Water.

Sample	Measured dpm	Measured dpm dpm in 10 uL	Extraction Efficiency
10-uL TCDD Standard	961.2	-	-
1	883.1	0.9187	91.87%
2	963.3	1.002	100.2%

Table 4. Results of Experiments to Determine Wall- and Cap Liner-Losses of T_4CDD from Water.

Sample	Percent Loss to Walls
1	2.8
2	4.2
3	3.2
4	3.4
5	4.7
6	2.8
Average	3.5
Standard Deviation	0.8

was made to determine the fraction of this material which was associated with the soil fines which were observed to be retained by the walls and liner, and experimental values of C and S were not corrected to account for these apparent losses.

PCP Screening Experiments

Preliminary experiments were conducted to validate mass balances and the centrifugation procedure used to evaluate sorption of PCP.

Mass balance experiments were conducted with and without soil to assess recovery of PCP. These tests were performed using the general batch shake test procedure, except that PCP associated with the entire liquid phase, soil phase, foil and teflon cap-liners and internal centrifuge walls was analyzed by LSC. Total liquid phase was withdrawn by pipet and added in three equal volumes to vials containing cocktail. The total soil phase and the Teflon/foil cap-liner was similarly analyzed by adding to cocktail. Container walls were rinsed with 3 1-mL volumes of methanol, all of which was added to cocktail. The results of these experiments indicated that PCP recovery was essentially 100%, and that sorptive losses to tube walls and cap liners were negligible.

Centrifugation at 3,000 rpm for 10 minutes and 30 minutes resulted in no differences in observed sorption of PCP, and hence a centrifugation time of 10 minutes was used prior to liquid-phase sampling.

Kinetic Evaluations

Time series experiments involving sorption of PCP from water by soils 91 and 96 and sorption of P_5CDD and O_8CDD by the two aquifer materials were conducted to qualitatively evaluate sorption kinetics and primarily to determine the contact time necessary to attain sorption equilibrium.

Experiments involving PCP were conducted by using 0.3 g of soil and a PCP dose such that initial concentration in the liquid phase was 0.035 ug/mL. The liquid volume used in these experiments was 15-17 mL as necessary to completely fill the centrifuge tube in order to minimize volatile losses of PCP into the headspace of the tube. Total liquid volume in each tube was determined gravimetrically. Tubes were contacted for various times (1, 2, 4 and 7 hours and 2, 3, 5, 17 and 31 days). Tubes were prepared in triplicate for each of the noted contact periods. After contacting, the liquid phase of each tube was sampled for pH and LSC analysis.

Experiments involving the aquifer materials utilized contact periods of 2-72 hr. These experiments were performed at f_s of 0.25 for P_5CDD and f_s of 0.65 for O_8CDD. P_5CDD and O_8CDD were chosen on the basis of kinetic data for surface soils presented by Guiseppi-Elie (1987) which indicated that these PCDDs bound the kinetic behavior of all PCDDs studied (i.e., most and least rapid approach to equilibrium, respectively). The noted f_s values for each PCDD correspond to the lowest f_s for which batch isotherm experiments were conducted. It was anticipated that experiments involving these f_s values would provide a conservative estimate of the contact time required to achieve sorption equilibrium because the kinetic data of Guiseppi-Elie (1987) indicated that the contact time necessary to achieve sorption equilibrium increased with decreasing f_s.

Equilibrium Evaluations

Sorption isotherm experiments generally consisted of fifteen tubes, in which five solute doses were delivered to triplicate tubes.

Experiments Involving Diesel Fuel

Preliminary experiments were conducted to evaluate the feasibility of using batch techniques to study the sorption of

PCDDs in the presence of diesel fuel. These experiments were conducted by precoating 0.3 g of soil with 1 mL of diesel fuel and adding the precoated soil to 12 mL of liquid phase in a centrifuge tube. Tubes were contacted for 24 hours, and were subsequently centrifuged for various times (10, 20, 30 and 60 minutes) at 3,000 rpm to qualitatively evaluate emulsion formation and separability.

SATURATED-FLOW SOIL COLUMN TESTING

Saturated-flow soil column testing was performed to validate the use of the column techniques for estimating K_D of the PCDDs. These column techniques were then applied to study the sorption of PCDDs in the presence of PCP and CB. These experiments were conducted by using the system depicted in Figure 2. The system was comprised of a Model LC-2600 syringe pump obtained from Isco (Lincoln, NB), a six-way injection valve obtained from Valco (Houston, TX), a soil column and a Retriever II fraction collector obtained from Isco. The syringe pump had an operating flow rate range of 0.03-200 mL/hr and a solvent reservoir volume of 260 mL. The fraction collector was capable of collecting samples in either a time or drop mode.

Two soil columns were used. Most of the experiments were conducted by using a glass column (2.5 cm x 25 cm) fitted with an adjustable plunger to accomodate variable soil masses in the column. Some experiments were conducted using a stainless steel column with an inner diameter of 48 mm (3/16 in) and 10 cm length. The range in liquid-phase pore velocity which could be achieved with the syringe pump and each of these columns was 0.003-20 and 0.06-380 m/day, respectively. These operating pore velocities are reasonable compared to typical groundwater velocities of 0.09-4.3 m/day (Bower, 1978).

The lengths, outer diameters and compositions of tubing used for plumbing connections between the components of the soil column system were: syringe pump to three-way valve, 15 cm (6

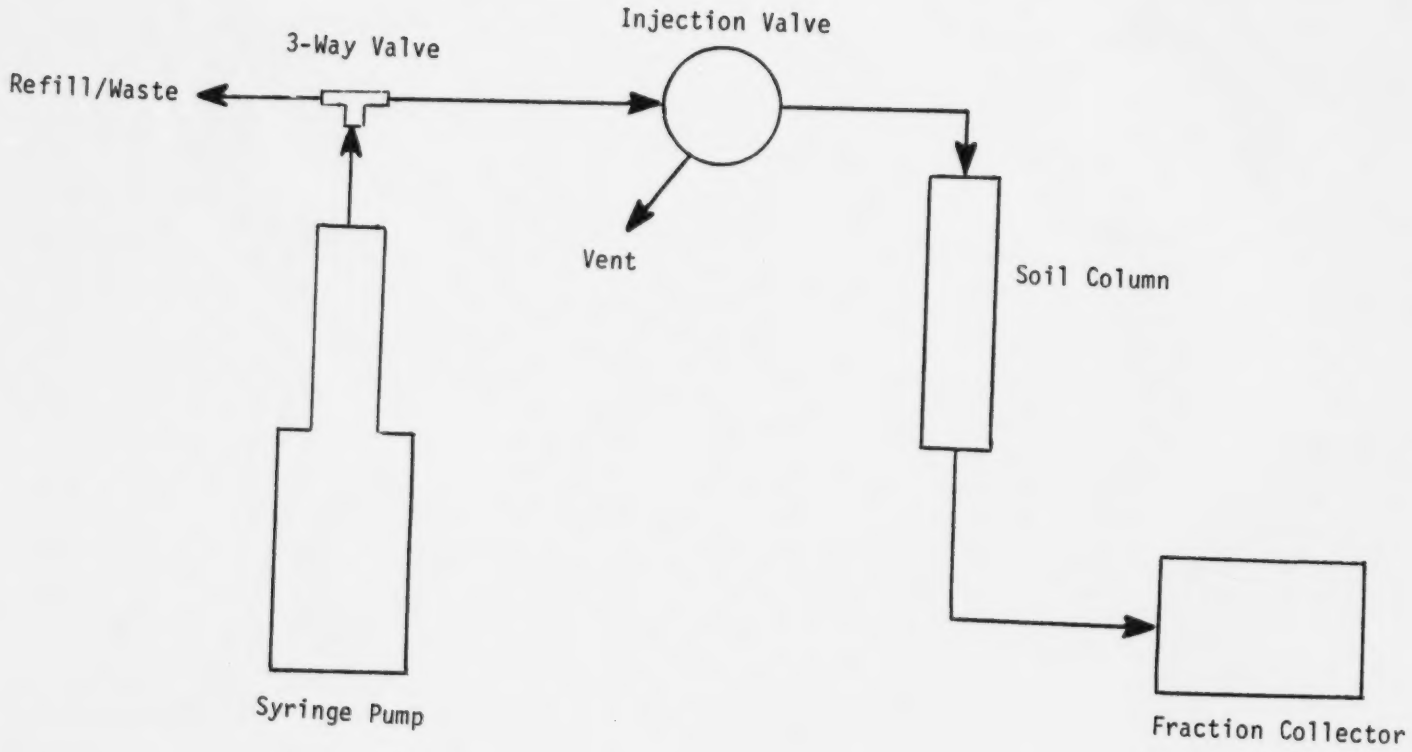

Figure 2. Schematic Diagram of the Saturated-Flow Soil Column System.

in) of 0.32 cm (1/8 in) stainless steel; three-way valve to injection valve, 20 cm (8 in) of 0.32 cm stainless steel and 20 cm of 0.16 cm (1/16 in) Teflon; injection valve to soil column, 30 cm (12 in) of 0.16 cm Teflon; and soil column to fraction collector, 20 cm of 0.16 cm Teflon. The inner diameters of the stainless steel and Teflon tubing were 0.16 cm (1/16 in) and 0.08 cm (1/32 in), respectively.

Column Packing

The 2.5 cm x 25 cm glass column was slurry packed by adding a known mass of soil (15-25 g) to roughly 20 mL of liquid phase in a 50-mL beaker, and by slowly pouring portions of the slurry into the top of the column. Solvent was allowed to flow from the column by gravity, and small amounts of slurry or fresh solvent were continuously added to the top of the column to maintain a liquid level above the soil at all times. The soil column was continously stirred using a glass stirring rod to help eliminate air bubbles from the soil bed and to pack the bed as uniformly as was possible.

The 48 mm x 10 cm stainless steel column was dry packed with a known mass of soil (2-3 g) with the aid of a vacuum pump.

The bulk density of soil in either column (ρ_B in equation (7)) was determined by dividing the mass of the soil added to the column by the total internal volume of the column occupied by soil.

Either soil column was conditioned with a minimum of 10 bed volumes of liquid phase prior to conducting experiments.

Pore Volume Determination

C-14 labeled methanol and H-3 labeled water were used as inert (nonsorbing) tracers for determination of the hydraulic detention volume (HDV) of the soil column. System flow rate was

set and 10-100 uL volumes of tracer were loaded via the injector valve. Effluent samples of 1 mL volume were collected directly into scintillation vials containing cocktail by using the fraction collector. Two or three bed volumes of liquid were passed through the column following injection of the tracer, and all of the effluent was collected as consecutive increments to enable determination of tracer recovery by mass balance. A plot of effluent concentration versus cumulative effluent volume was prepared, and HDV was determined from this plot by using the center-of-mass of the effluent tracer peak.

The soil column void fraction (ε in equation (7)) was determined by dividing HDV by total internal column volume.

Solute Retention Experiments

Column retardation experiments involving sorbing solute were conducted by pulse input of the radiolabeled solute in a manner similar to that employed to evaluate column HDV. The experiments were conducted by collecting all of the effluent samples to enable determination of solute recovery by mass balance. Flow rate was maintained by the syringe pump control and was checked gravimetrically by measuring the mass of column effluent collected over the period of time involved. A plot of effluent sample concentration versus cumulative effluent volume was prepared, and the solute retention volume was determined by the center-of-mass of the effluent solute peak. The retardation factor (i.e., $1/V_r$ in equation (7)) was calculated by dividing solute retention volume by column HDV. The apparent or observed partition coefficient (K_{obs}) was calculated using equation (7), and the measured values of ρ_B, ε and $1/V_r$.

Diesel Fuel

An experiment involving diesel fuel was conducted by packing the stainless steel column with soil saturated with diesel fuel.

The soil (roughly 3 g) was precoated by adding sufficient diesel fuel to thoroughly wet the soil (roughly 3 mL). The soil and diesel fuel were mixed in a 50-mL beaker using a spatula until a uniform consistency was achieved. The precoated soil was added to the column in small increments, and the soil bed was periodically compacted manually using a stirring rod. Liquid flow rates of 0.16, 0.8 and 8.0 mL/hr were utilized to elute the diesel fuel, and effluent samples were collected in glass tubes and were analyzed for turbidity.

SECTION 7

RESULTS AND DISCUSSION

SOLUBILITY DETERMINATIONS

The results of experiments to determine the solubility of P_5CDD, H_6CDD, H_7CDD and O_8CDD in methanol are summarized in Table 5. Included in Table 5 are the solubility data of Yousefi (1986) for T_4CDD in methanol and the results of experiments to determine the solubility of P_5CDD and PCP at f_s of 0.5.

Values of σ_s determined from the solubility data for each of the PCDDs and for PCP are also listed in Table 5. These values represent the slope of the log-linear relationship between X_i and f_s in equation (10). For the PCDDs, values of σ_s were calculated by using the methanol solubility data in Table 5 and water solubility for the PCDDs reported by Marple et al. (1986a) for T_4CDD and by Friesen et al. (1985) for the other PCDDs, and by assuming that the log-linear relationship applies between these endpoints. For PCP, σ_s was calculated by linear regression using the solubility data for PCP in water and in methanol of 80 mg/L (Merck, 1983) and 180 g/L (Crosby et al., 1981), respectively, and the value reported in Table 5 for f_s of 0.5.

SORPTION TO SURFACE SOILS

Sorption of PCP

The results of times series experiments to evaluate the kinetics of sorption of PCP from water to soils 91 and 96 are plotted in Figure 3. These results suggest that equilibrium for sorption of PCP to soil 91 was achieved in less than one day of contact, while a thirty-day contact period was necessary for equilibrium to be achieved for sorption of PCP to soil 96.

Table 5. Summary of Results for Solubility Determinations for PCDDs and PCP in Water/Methanol Mixtures.

	Measured Solubility, mg/L			σ_s
f_s	0.0	0.50	1.0	
T_4CDD[a]				
Mean	16×10^{-6}		10.6	6.25
St. Dev.			0.5	
n			33	
P_5CDD[b]				
Mean	120×10^{-6}	0.10	52	6.09
St. Dev.		0.2	2	
n		18	6	
H_6CDD[b]				
Mean	4.4×10^{-6}		20	7.01
St. Dev.			2	
n			15	
H_7CDD[b]				
Mean	2.4×10^{-6}		24	7.35
St. Dev.			2	
n			12	
O_8CDD[b]				
Mean	0.4×10^{-6}		4.0	7.35
St. Dev.			0.6	
n			56	
PCP[c]				
Mean	80	3.1×10^3	180×10^3	3.8
St. Dev.		0.6		
n		9		

[a]Water solubility reported by Marple et al. (1986a).

[b]Water solubility reported by Friesen et al. (1985).

[c]Water and methanol solubilities reported by Merck (1984) and Crosby et al. (1981), respectively.

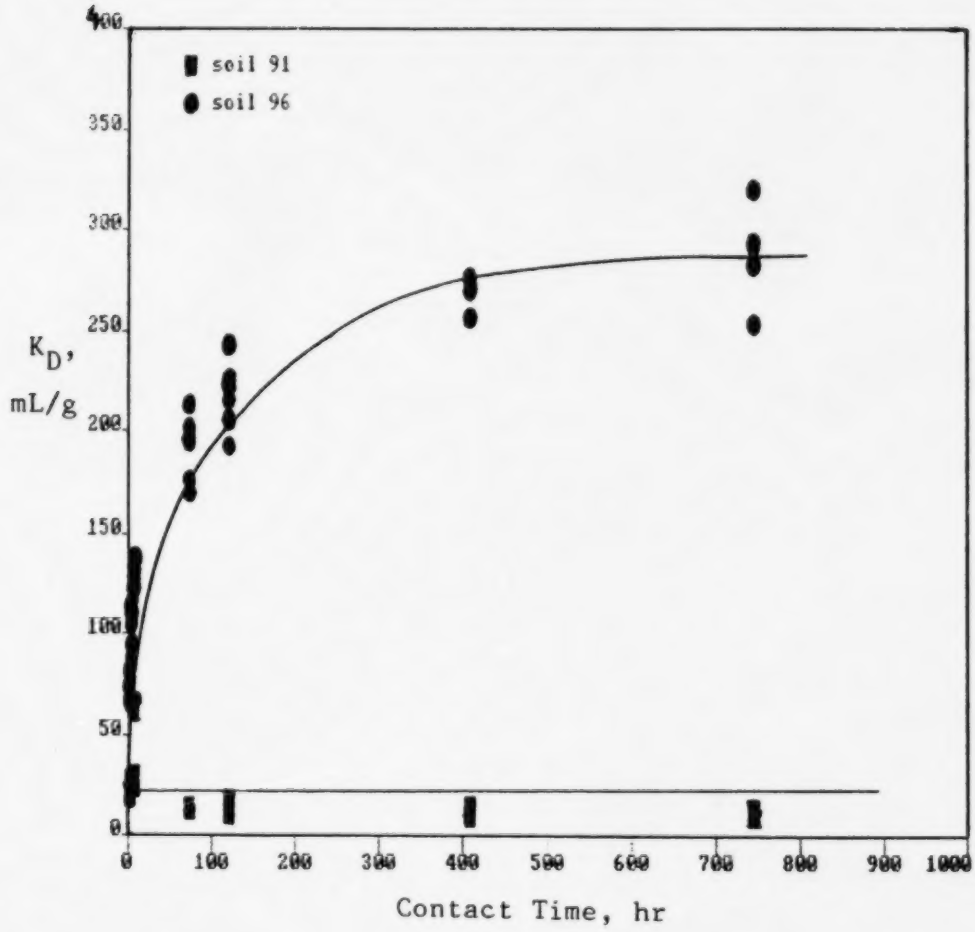

Figure 3. Plot of K_D Versus Contact Time for Sorption of PCP from Water by Soils 91 and 96.

Equilibrium isotherm data for the sorption of PCP by soils 91 and 96 were generated by batch techniques at f_s of 0.0, 0.25 and 0.5 and for soil 96 at f_s of 0.75. Contact periods of 2 and 30 days were used for soils 91 and 96, respectively. An isotherm plot for sorption of PCP by soils 91 and 96 from water is shown in Figure 4. Similar linear isotherm plots were obtained for sorption of PCP by these soils at other f_s. The results of regression analysis of the isotherm data obtained for all f_s studied are summarized in Table 6.

K_{obs} values for sorption of PCP by soil 91 were also estimated from column experiments. An effluent concentration profile for PCP at f_s of 0.0 (water) is shown in Figure 5. This peak, which is slightly skewed to the right, was typical of concentration profiles obtained at other f_s. The tailing deomonstrated by the plot in Figure 5 became less significant as f_s was increased. K_{obs} values were determined by using equation (7) and an average solute velocity as characterized by the center-of-mass of the effluent peak. Values of K_{obs} estimated in this way are listed in Table 7.

Values of $\log(K_{m,oc})$ for sorption of PCP by soils 91 and 96 listed in Tables 4 and 5 are plotted versus f_s in Figure 6. The results obtained from batch and column techniques are in reasonable agreement over the entire range in f_s studied. Regression parameters and statistics determined from regression analysis of the data in Figure 6 according to equation (8) are summarized in Table 8. The results of regression analysis of the combined data (i.e., both soils and both techniques) are expressed in equation (16):

$$\log(K_{m,oc}) = -3.29f_s + 2.32 \qquad r^2 = 0.94 \qquad s = 1.93 \qquad (16)$$

The slope of equation (16) represents the product of α and σ_s. Using the value of σ_s of 3.8 presented in Table 5 determined for PCP, the apparent value of α from the combined

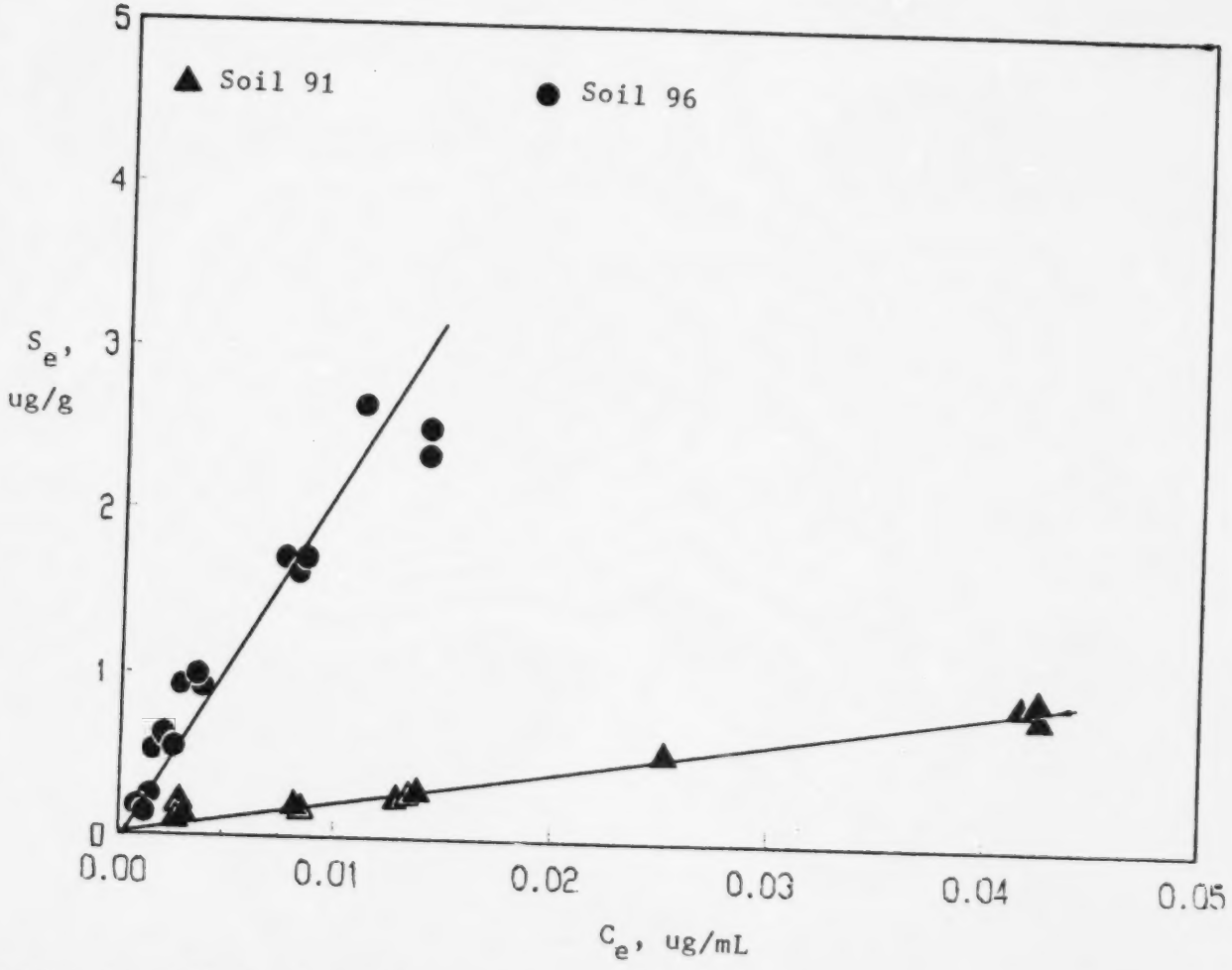

Figure 4. Plot of S_e Versus C_e for Sorption of PCP from Water by Soils 91 and 96.

Table 6. Summary of Isotherm Parameters Determined for Sorption of PCP by Soils 91 and 96.

	Volume Fraction Methanol, f_s				
Soil 91	0.0	0.25[b]	0.25[b]	0.5	0.75
K_D, mL/g	18	4.5	5.0	1.1	
r^2	0.999	0.93	0.93	0.69	
n	12	13	14	7	
pH[a]	7.0	6.5	6.9	6.5	
$K_{m,oc}$, mol/g	150	33	37	6.9	
$\log(K_{m,oc})$	2.18	1.52	1.57	0.84	
Soil 96					
K_D, mL/g	180	96		12	2.0
r^2	0.96	0.98		0.98	0.60
n	14	15		15	8
pH[a]	6.6	6.3		6.2	6.0
$K_{m,oc}$, mol/g	130	61		6.5	0.87
$\log(K_{m,oc})$	2.11	1.78		0.81	-0.06
Molar Volume, mL/mol	18.0	20.5	20.5	24.1	29.8

[a]pH is the value of the pH in solution at the end of the contact period.

[b]Replicate isotherms for soil 91 at fs of 0.25 were determined for contact periods of 2 days and 4 days, respectively.

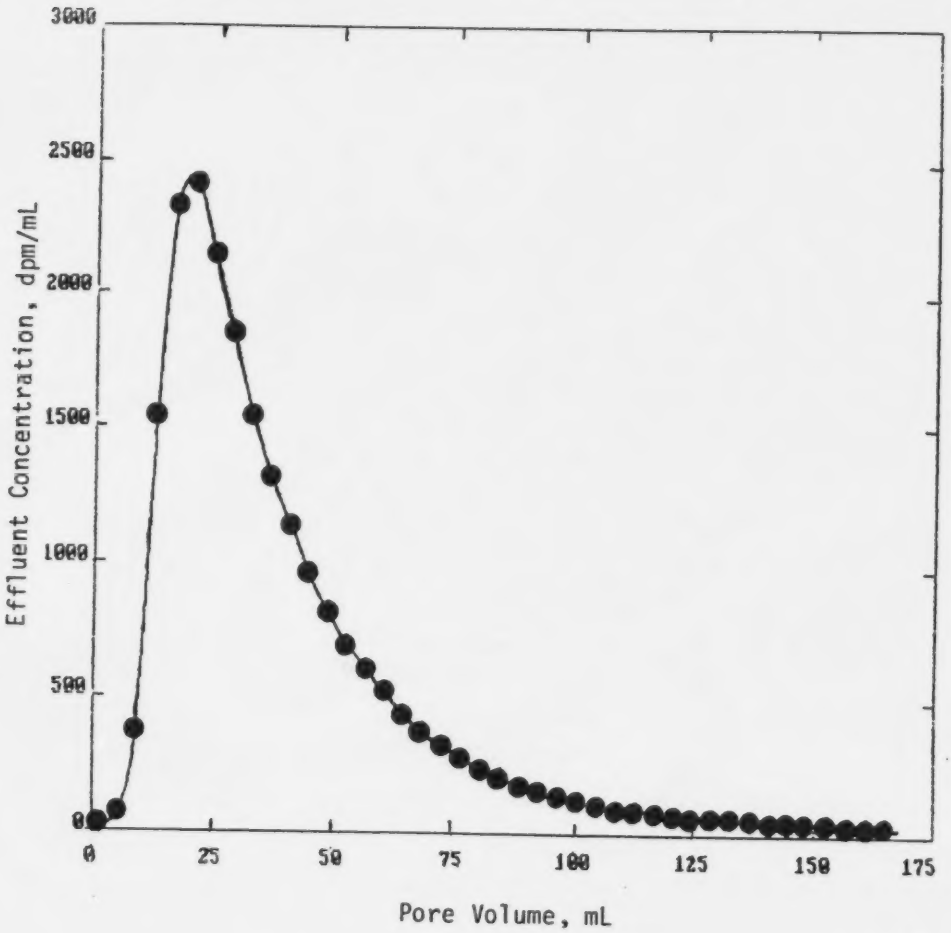

Figure 5. Plot of Effluent Concentration Versus Cumulative Effluent Volume for Pulse Input of PCP in Water to Column Containing Soil 91.

Table 7. Summary of K_{obs} Values Determined for Sorption of PCP by Soil 91.

f_s	0.0	0.25	0.5	0.75	0.9
ρ_B, g/mL	1.4	1.4	1.4	1.4	1.8
	0.79	0.79	0.79	0.79	0.51
K_{obs}, mL/g	13	11	0.56	0.10	0.03
Column residence time, min	21	11	11	11	47
Mass of PCP recovered, %	95	90	100	95	99
Molar Volume, mL/mol	18.0	20.5	24.1	29.8	37.9
$K_{m,oc}$, mol/g	110	80	3.5	0.51	0.12
$\log(K_{m,oc})$	2.04	1.90	0.54	-0.29	-0.92
pH	7.1	6.9	6.7	6.9	7.0

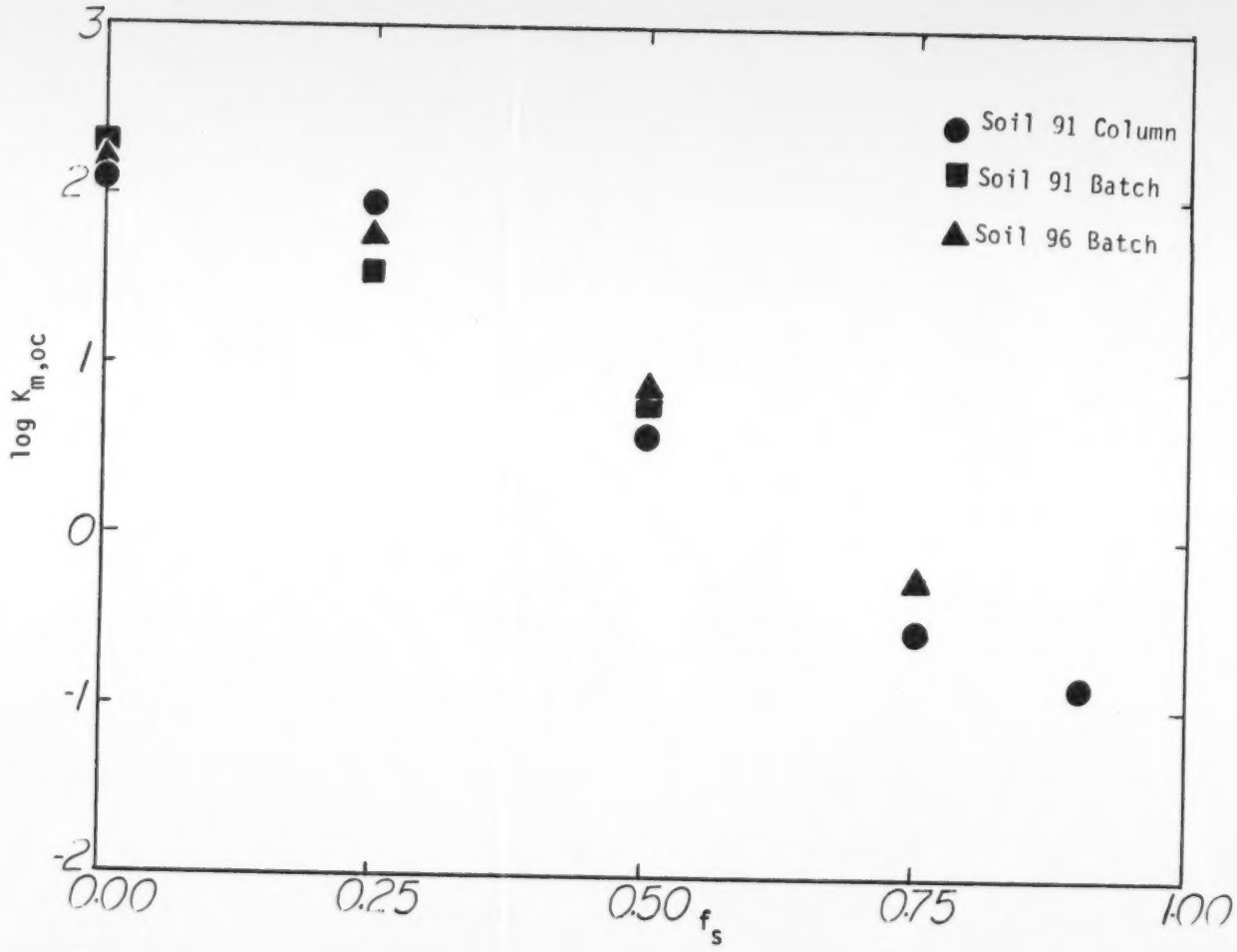

Figure 6. Log-Linear Plot of $K_{m,oc}$ Versus Volume Fraction Methanol for Sorption of PCP by Soils 91 and 96.

Table 8. Summary of Regression Parameters for Sorption of PCP by Soils 91 and 96 from Water/Methanol Mixtures.

	Soil 91, Batch	Soil 96, Batch	Soil 91, Column	Combined Data[a]
Slope, $\alpha\sigma_s$	2.68	2.99	3.51	3.29
Intercept, $\log(K_{m,oc,w})$	2.20	2.28	2.33	2.32
α	0.71	0.79	0.92	0.87
n	4	4	5	13
r^2	0.999	0.96	0.96	0.94
s	0.035	0.23	0.31	1.9

[a]Data from the three soil/technique data sets were combined and regressed on the basis of no consistent relative trend demonstrated by the individual data sets (i.e., neither data set gave consistently high or low values).

data is 0.87. These values of $\alpha\sigma_s$ and α are added to the plot presented by Walters and Guiseppi-Elie (1988) which is shown in Figure 7. The value of $\log(K_{ow})$ of 5.24 used to plot the data for PCP in Figure 7 is that reported by Schellenberg et al. (1984). Included in Figure 7 are data reported for the sorption to soils from water/methanol mixtures for several hydrophobic organic contaminants ranging in $\log(K_{ow})$ from 2.04-6.64 (Fu and Luthy, 1986; Nkedi-Kizza et al., 1985; Walters and Guiseppi-Elie, 1988). As is apparent from Figure 7, the values of α and $\alpha\sigma_s$ observed for PCP are consistent with the trend observed for other organic contaminants in which α and σ_s increase with increasing $\log(K_{ow})$.

Sorption of T_4CDD from Water

The sorption isotherm data for each of the two procedures used to evaluate sorption of T_4CDD by soil 91 from water are summarized in Tables 9 and 10. The sorption isotherm data for each of these experiments are plotted in Figure 8.

The value of $\log(K_{oc})$ determined from the experiment involving unwashed soil and a contact period of 48 hours was 6.44, while the value of $\log(K_{oc})$ determined from the experiment involving prewashed soils and a contact period of ten days was 6.66. The difference between the $\log(K_{oc})$ values determined in each of these experiments is not substantial (i.e., less than a factor of 2). However, the increased contact period and prewashing to remove nonseparable materials from the water phase apparently resulted in a value of $\log(K_{oc})$ which was slightly greater than that determined for the shorter contact period without prewashing.

The value of $\log(K_{oc})$ of 6.67 determined by the second procedure corresponds to a value of $\log(K_{m,oc})$ of 5.41. This value is plotted in Figure 9 along with the water/methanol data for T_4CDD and soils 91 and 96 of Walters and Guiseppi-Elie (1988). The experimental value of the water-phase partition

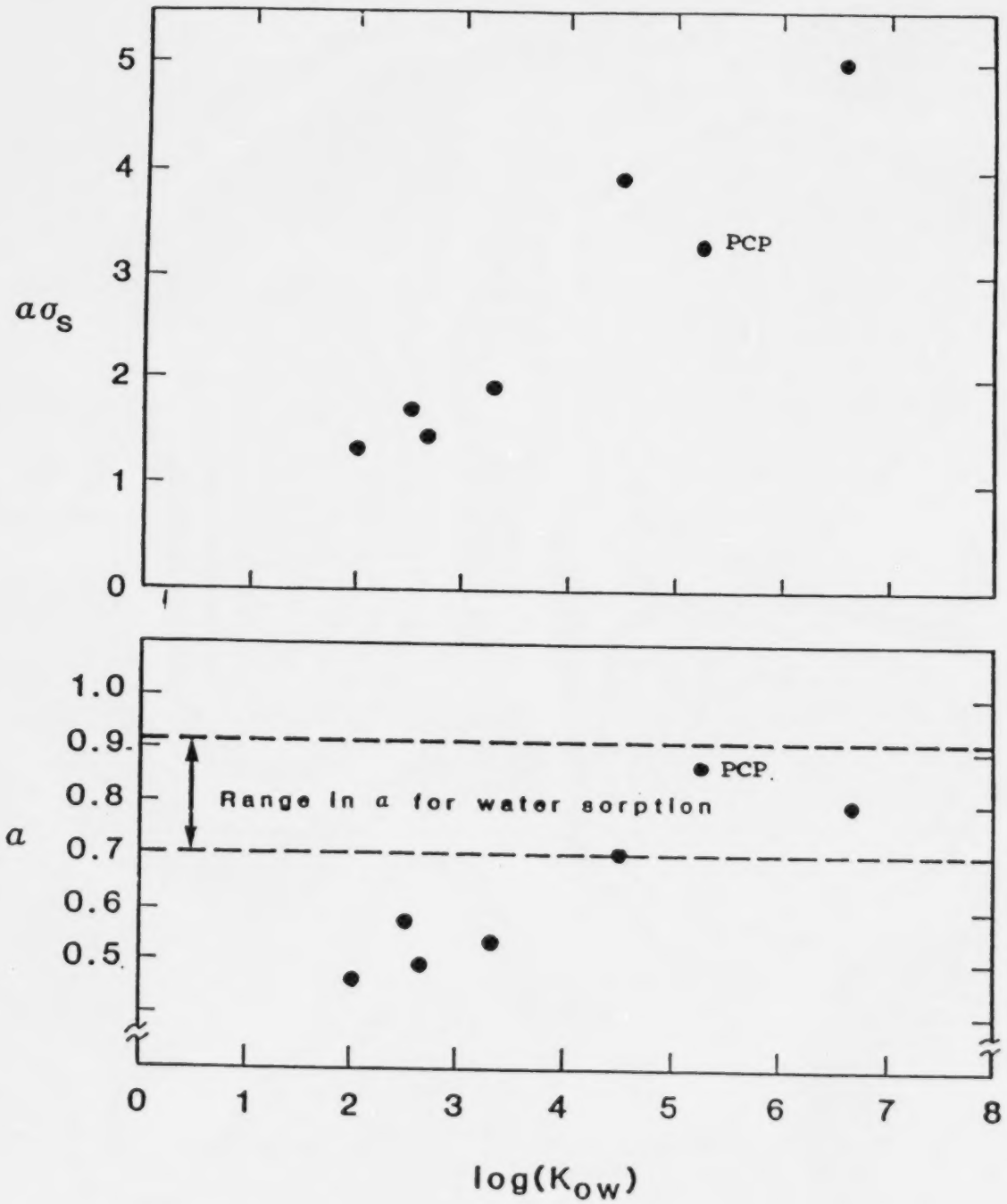

Figure 7. Plot of $a\sigma_s$ and a Versus Log(K_{ow}) for Sorption of Several Hydrophobic Organic Contaminants by Soils from Water/Methanol Mixtures.

Table 9. Isotherm Data for Sorption of T_4CDD by Soil 91 from Water for a Contact Period of Two Days.

Mass Soil, g	Total TCDD Dose, ug	C, ug/mL	S, ug/g
0.0521	0.0074	8.40×10^{-6}	0.136
0.0546	0.0074	8.30×10^{-6}	0.129
0.0511	0.0129	1.40×10^{-5}	0.241
0.0554	0.0129	1.60×10^{-5}	0.221
0.0521	0.0160	1.38×10^{-5}	0.305
0.0523	0.0160	1.37×10^{-5}	0.303

Table 10. Isotherm Data for Sorption of T_4CDD by Soil 91 from Water for a Contact Period of Ten Days.

Mass Soil, g	Total Mass TCDD, ug	C, ug/mL	S, ug/g
0.0325	0.0116	1.02×10^{-5}	0.324
0.0537	0.0116	6.90×10^{-6}	0.211
0.0544	0.0164	1.07×10^{-5}	0.294
0.0510	0.0164	1.02×10^{-5}	0.314
0.0496	0.0203	1.35×10^{-5}	0.398
0.0504	0.0203	1.21×10^{-5}	0.392

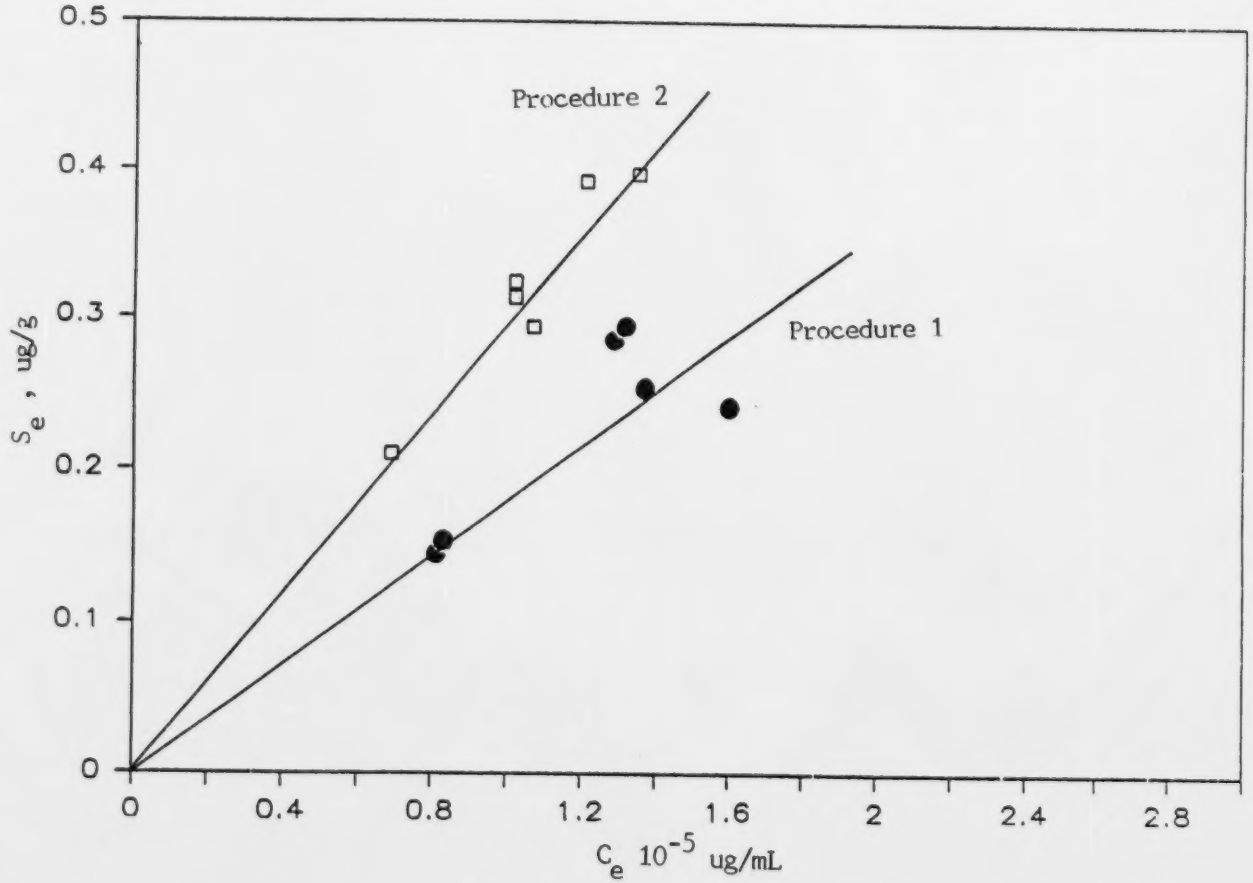

Figure 8. Plot of S_e Versus C_e for Sorption of T_4CDD by Soil 91 from Water.

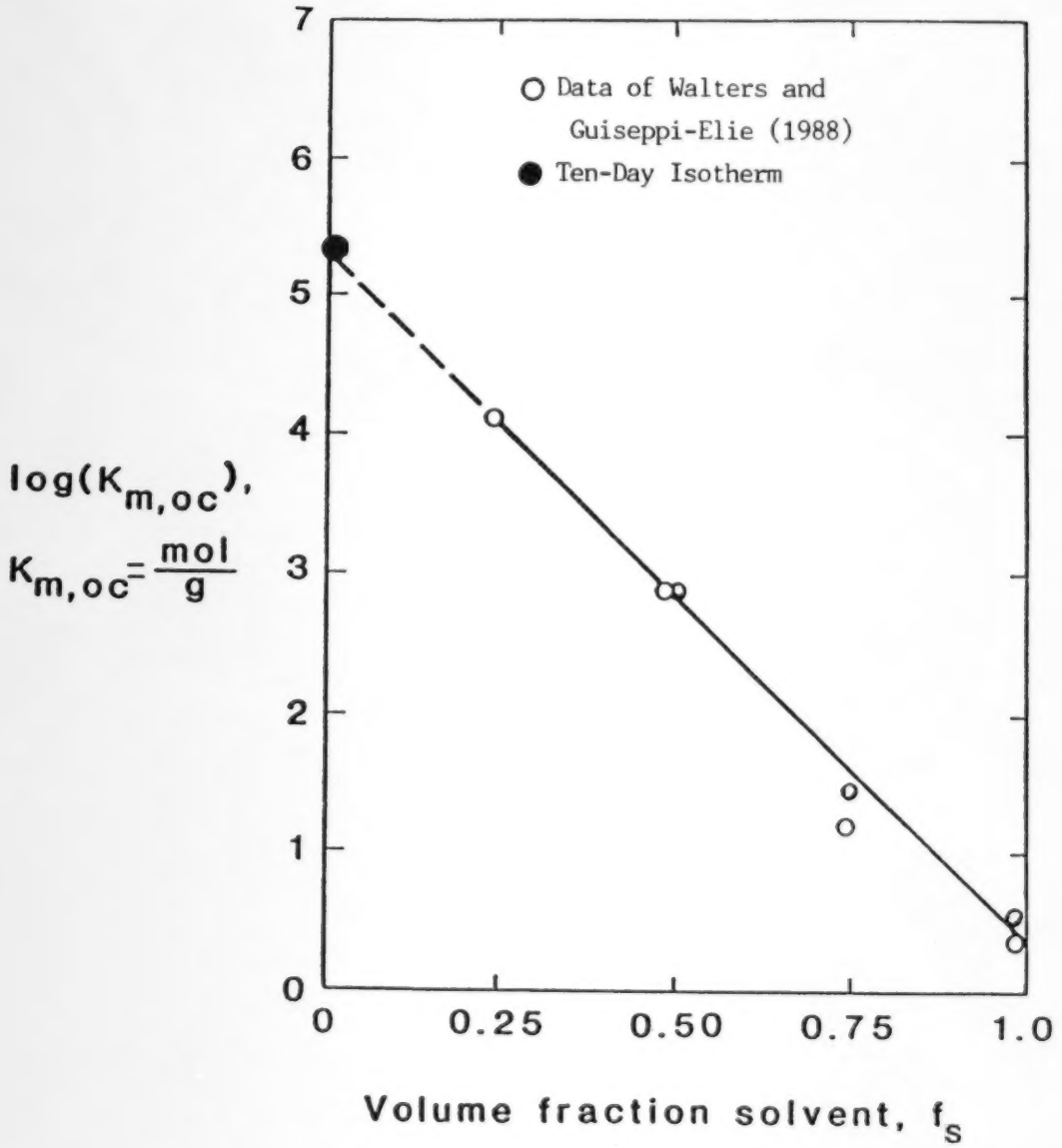

Figure 9. Log-Linear Plot of $K_{m,oc}$ Versus Volume Fraction Methanol for Sorption of T_4CDD by Soils 91 and 96 from Water/Methanol Mixtures.

coefficient is in good agreement with the value predicted by log-linear extrapolation of the water/methanol data ($\log(K_{m,oc})$ predicted is 5.30). Based on this observation, it appears that for T_4CDD the cosolvent theory of equation (8) applies over the entire range of f_s from 0.0-1.0 for water/methanol mixtures. This provides strong support for the validity of this theory to PCDDs and other highly-hydrophobic organic contaminants, and also provides support for the use of log-linear extrapolation to estimate water-phase K_{oc} values for PCDDs by using data generated for water/methanol mixtures.

Sorption of PCDDs from Mixtures
of Water and Methanol

The sorption of PCDDs by soils from water/methanol mixtures was studied to supplement the data of Guiseppi-Elie (1987) and to evaluate the relationship between K_Ds determined by batch versus column techniques for PCDDs other than T_4CDD. Batch experiments were conducted to evaluate sorption of all PCDDs at f_s of 0.9 for soil 91. Column experiments were conducted using soil 91 and f_s of 0.75, 0.90 and 1.0 for all PCDDs.

The results of the batch experiments to evaluate sorption isotherm data were typical of those for O_8CDD plotted in Figure 10. Linear sorption isotherms were observed for all PCDDs studied. Values of the regression parameters and statistics corresponding to these isotherms are listed in Table 11. The values of K_D shown in Table 11 for the four PCDDs are generally comparable (i.e., ranging from 1.8-3.8 mL/g) and do not show the expected trend of increasing with increasing hydrophobicity of the PCDD. However, it is noted that these K_D values are below the minimum value of 10 mL/g identified by Yousefi (1986) necessary to achieve "reasonable" experimental uncertainties (e.g., 15-20%) by batch techniques. Below this limit, column techniques are more appropriate for estimating K_D (Yousefi, 1986).

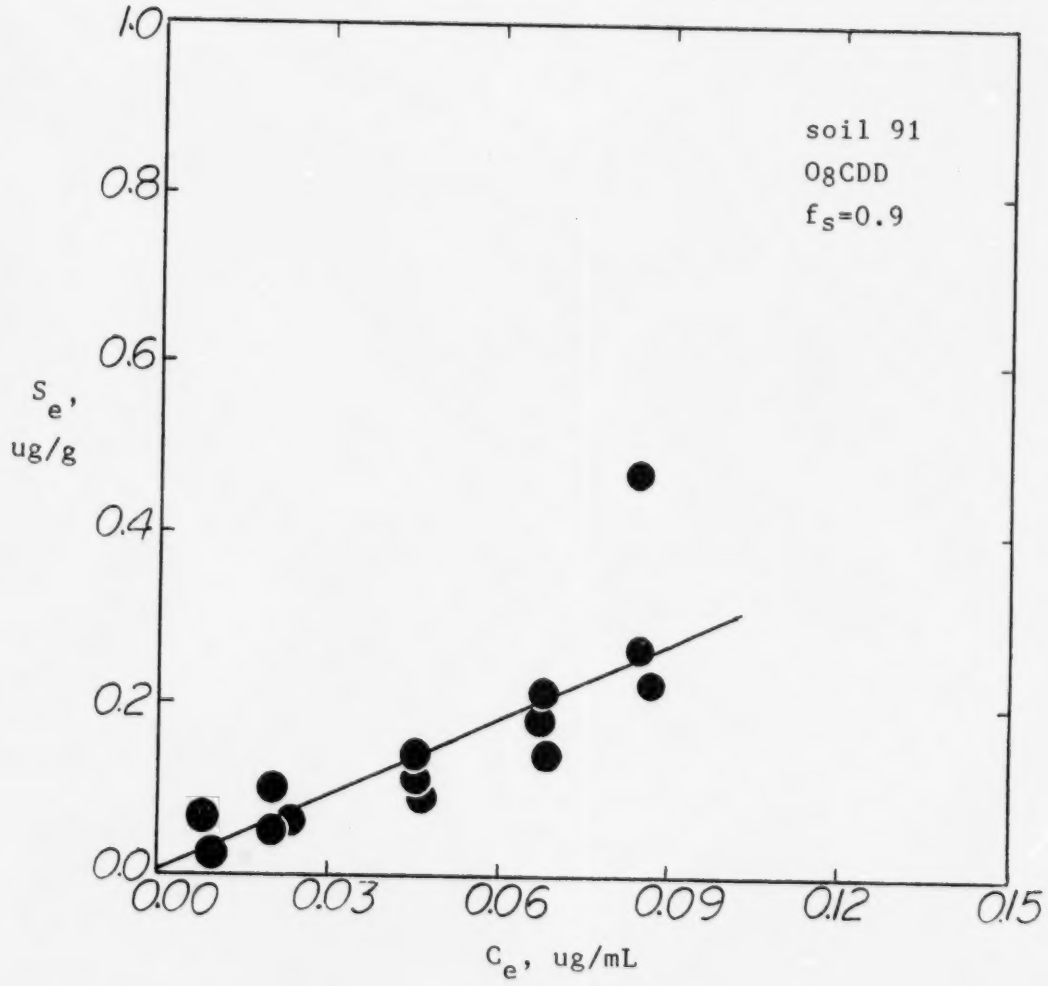

Figure 10. Plot of S_e Versus C_e for Sorption of O_8CDD by Soil 91 at f_s of 0.9 and Contact Time of Five Days.

Table 11. Summary of Isotherm Parameters Determined for Sorption of P_5CDD, H_6CDD, H_7CDD and O_8CDD by Soil 91 at f_s of 0.9.

	P_5CDD	H_6CDD	H_7CDD	O_8CDD
K_D, mL/g	3.8	2.3	1.8	3.0
r^2	0.92	0.83	0.83	0.88
n	6	15	15	14
$K_{m,oc}$, mol/g	15	9.1	7.5	12
$\log(K_{m,oc})$	1.18	0.96	0.88	1.08

The results of column experiments are presented in Table 12. Information in Table 12 includes all measured values necessary to calculate K_{obs} according to equation (7).

The values of K_D and K_{obs} determined for the PCDDs by batch and column techniques, respectively, were normalized on f_{oc} and converted to molar units by dividing by liquid-phase molar volume. The logarithm of these values, listed in Tables 11 and 12, are plotted in Figures 11-14 versus f_s. Also plotted for reference purposes are the batch data of Guiseppi-Elie (1987) obtained using soil 91 and the corresponding PCDD. The results of the batch experiments determined in the present study are in general agreement with the log-linear relationship based on the data of Guiseppi-Elie (1987). However, the results obtained by column techniques were consistently lower than expected from the log-linear relationship of the batch data only.

It is not suspected that soil-solvent effects (i.e., extraction of soil organic matter by the methanol) were responsible for the observation that the K_{obs} values (determined by column) were lower than K_D values (determined by batch). Column retardation factors were determined in the present study by using both "fresh" and "aged" soils (viz., soils which were not previously leached with methanol and soils which were previously leached with 10-20 bed volumes of methanol). The results of these studies indicated that retardation factors were essentially independent of the volume of methanol previously passed through the soil column.

The relatively low values of K_{obs} in comparison to K_D were believed to be attributed to non-attainment of local equilibrium within the soil column for the flow rates utilized. This is suggested by the data presented in Table 12 at f_s of 1.0, which indicate that values of K_{obs} were slightly yet consistently lower at the higher flow rate. These differences might be expected on the basis of the different relative contact times of the respective experiments; batch experiments utilized contact

Table 12. Summary of K_{obs} Values Determined for Sorption of P_5CDD, H_6CDD, H_7CDD and O_8CDD by Soil 91 from Water/Methanol Mixtures.

	Volume Fraction Methanol, f_s		
	0.75[a]	0.9[b]	1.0[c]
Molar Volume, mL/mol	29.8	37.9	40.4
P_5CDD			
K_{obs}, mL/g	1.7	0.20	0.072, 0.057
$K_{m,oc}$, mol/g	8.6	0.79	0.27, 0.21
$\log(K_{m,oc})$	0.93	-0.10	-0.57, -0.68
H_6CDD			
K_{obs}, mL/g	3.6	0.23	0.10, 0.092
$K_{m,oc}$, mol/g	18	0.91	0.38, 0.35
$\log(K_{m,oc})$	1.3	-0.04	-0.42, -0.46
H_7CDD			
K_{obs}, mL/g	4.8	0.40	0.12, 0.11
$K_{m,oc}$, mol/g	24	1.6	0.45, 0.41
$\log(K_{m,oc})$	1.38	0.20	-0.35, -0.39
O_8CDD			
K_{obs}, mL/g		0.82	0.21, 0.19
$K_{m,oc}$, mol/g		3.2	0.79, 0.71
$\log(K_{m,oc})$		0.51	-0.10, -0.15

[a]Experiments were conducted at a column flow rate of 8 mL/hr (pore velocity of 13.5 m/day), with ρ_B of 1.4 g/mL and ε of 0.79.

[b]Experiments were conducted at a column flow rate of 8 mL/hr (pore velocity of 0.77 m/day), with ρ_B of 1.8 g/mL and ε of 0.51.

[c]Experiments were conducted at column flow rates of 12 mL/hr and 20 mL/hr (pore velocities of 1.78 and 2.96 m/day), respectively, with ρ_B of 1.75 g/mL and ε of 0.33.

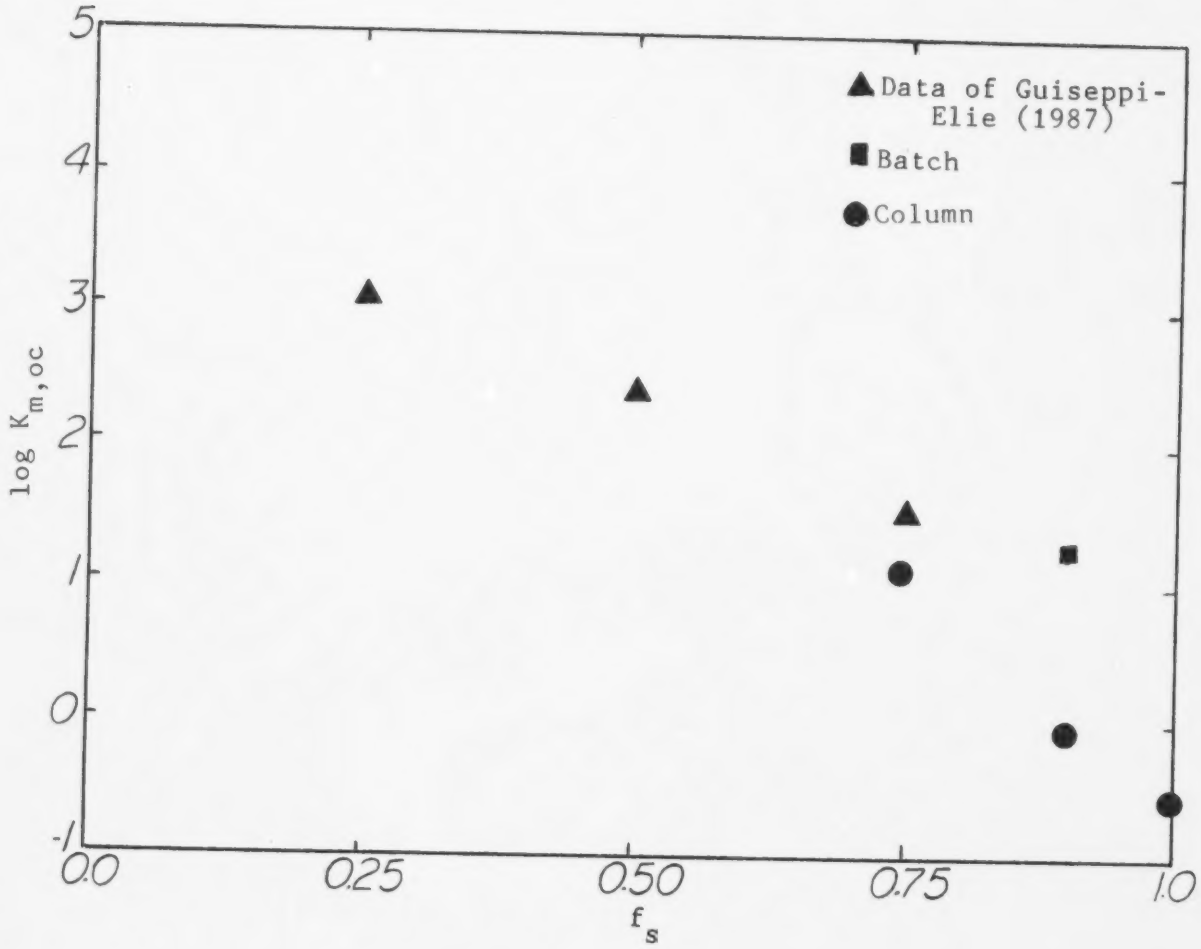

Figure 11. Log-Linear Plot of $K_{m,oc}$ Versus Volume Fraction Methanol for Sorption of P_5CDD by Soil 91.

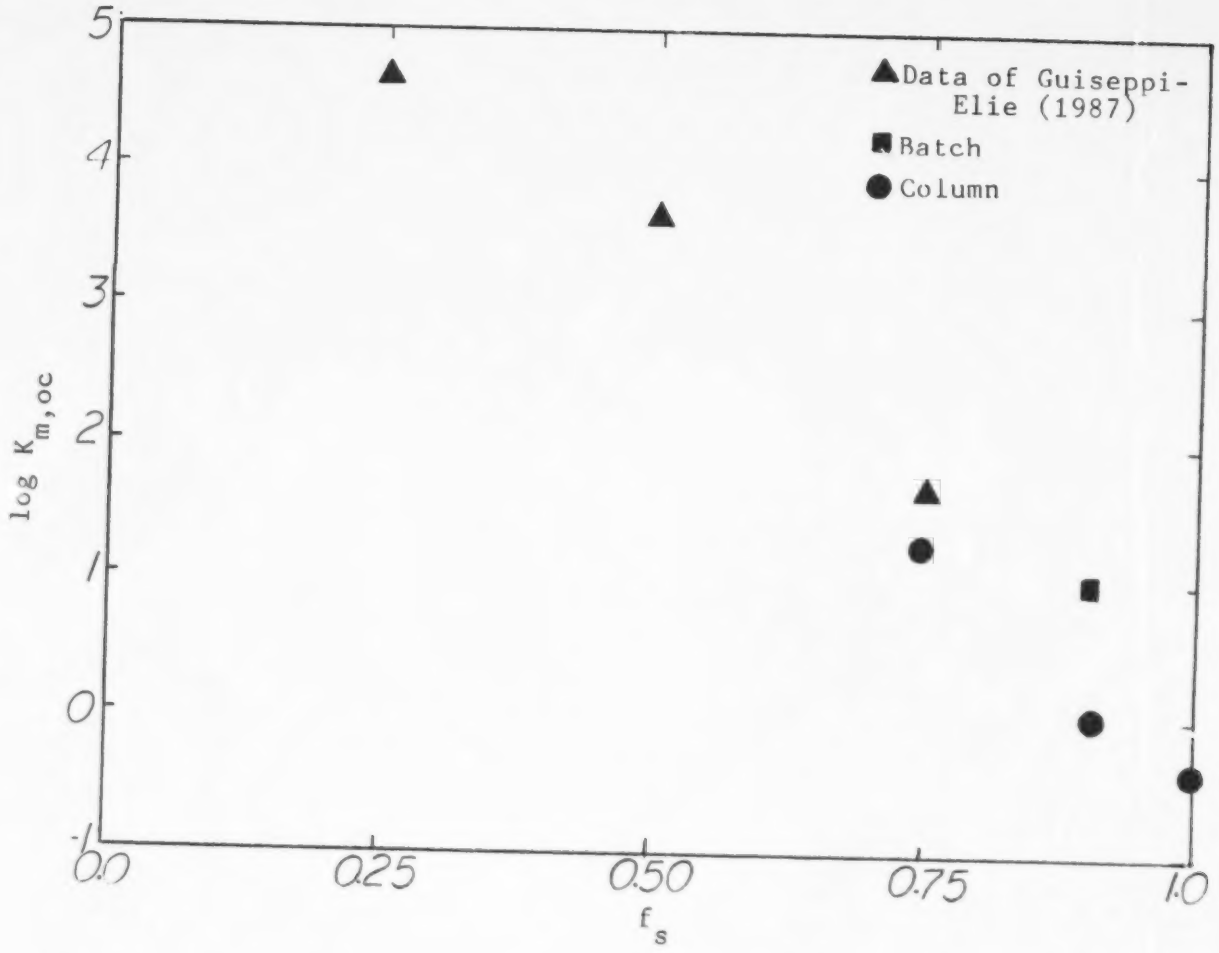

Figure 12. Log-Linear Plot of $K_{m,oc}$ Versus Volume Fraction Methanol for Sorption of H_6CDD by Soil 91.

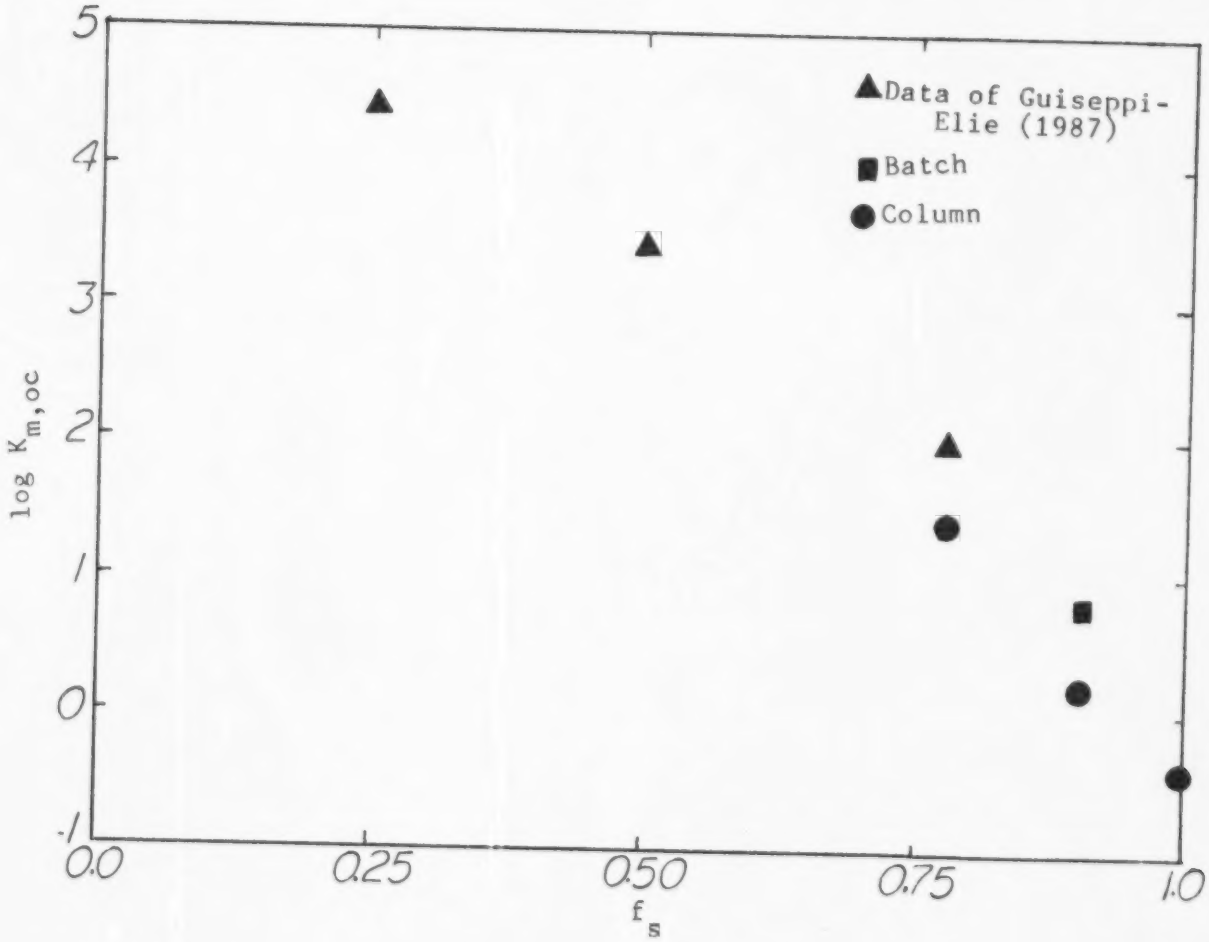

Figure 13. Log-Linear Plot of $K_{m,oc}$ Versus Volume Fraction Methanol for Sorption of H_7CDD by Soil 91.

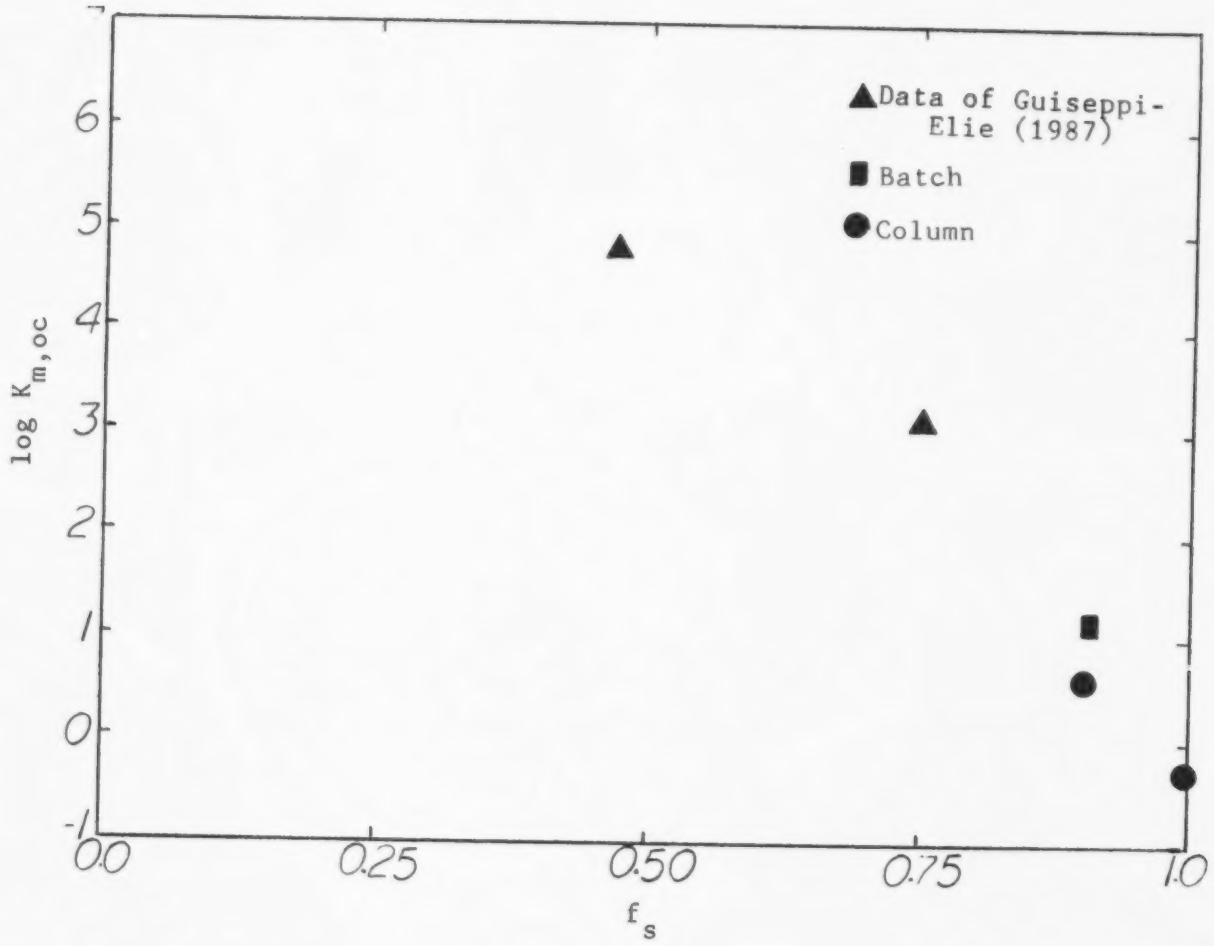

Figure 14. Log-Linear Plot of $K_{m,oc}$ Versus Volume Fraction Methanol for Sorption of O_8CDD by Soil 91.

periods of 5 days, while an average column residence time for the injected pulse of PCDD was 0.18-0.79 hr.

In an attempt to further assess the relationship between K_D and K_{obs}, the effect of column flow rate on K_{obs} for soil 91 and O_8CDD at f_s of 1.0 was studied. O_8CDD was selected for these studies because of the relatively slow sorption kinetics for this solute relative to the other PCDDs, and because it was suspected that the difference between K_D and K_{obs} might be primarily a result of kinetic limitations. Experiments were conducted using a 15-g soil column and liquid-phase flow rates of 0.4, 0.8, 2.0, 8.0, 12.0, 20.0 and 40.0 mL/hr (these values correspond to pore-liquid velocities of 0.06-5.9 m/day, and to column residence times of 0.18-18 hr). The K_{obs} values determined from these experiments are listed in Table 13 and plotted in Figure 15. Liquid-phase flow rate was not found to affect K_{obs} for flow rates in the range of 8-40 mL/hr. However, below this range K_{obs} was found to increase at lower flow rates. K_{obs} values determined at flow rates of 8-40 mL/hr were 34% of the maximum value of K_{obs} (0.58 mL/g) determined at a flow rate of 0.4 mL/hr. This K_{obs} value is in good agreement with the K_D value of 0.51 mL/g estimated by log-linear extrapolation of the batch data presented by Guiseppi-Elie (1987) for soil 91 and O_8CDD at f_s of 0.5 and 0.75 and that presented in Table 11 at f_s of 0.9. An explanation for this observation is not known at this time, though it is suspected that this observation may be explained in terms of relatively rapid sorption to external portions of the soil organic matter versus relatively slow sorption to organic matter which is associated with internal pores of the soil. Similar theories have been proposed to explain the kinetics for sorption to soils (Karickhoff, 1984).

Sorption of PCDDs in the Presence of PCP and CB

The effect of the presence of PCP on the sorption of PCDDs was evaluated by batch and column techniques.

Table 13. Summary of K_{obs} Values Determined for O_8CDD by the Soil Column Technique as a Function of Liquid Phase Flow Rate.

Flow Rate, mL/hr	Pore Velocity, m/day	$1/V_r$	K_{obs}, mL/g
0.4	0.06	4.08	0.58
0.8	0.12	3.15	0.40
2.0	0.30	2.98	0.37
2.0	0.30	2.85	0.35
8.0	1.19	2.02	0.19
12.0	1.78	2.13	0.21
20.0	2.97	2.00	0.19
40.0	5.94	2.10	0.21

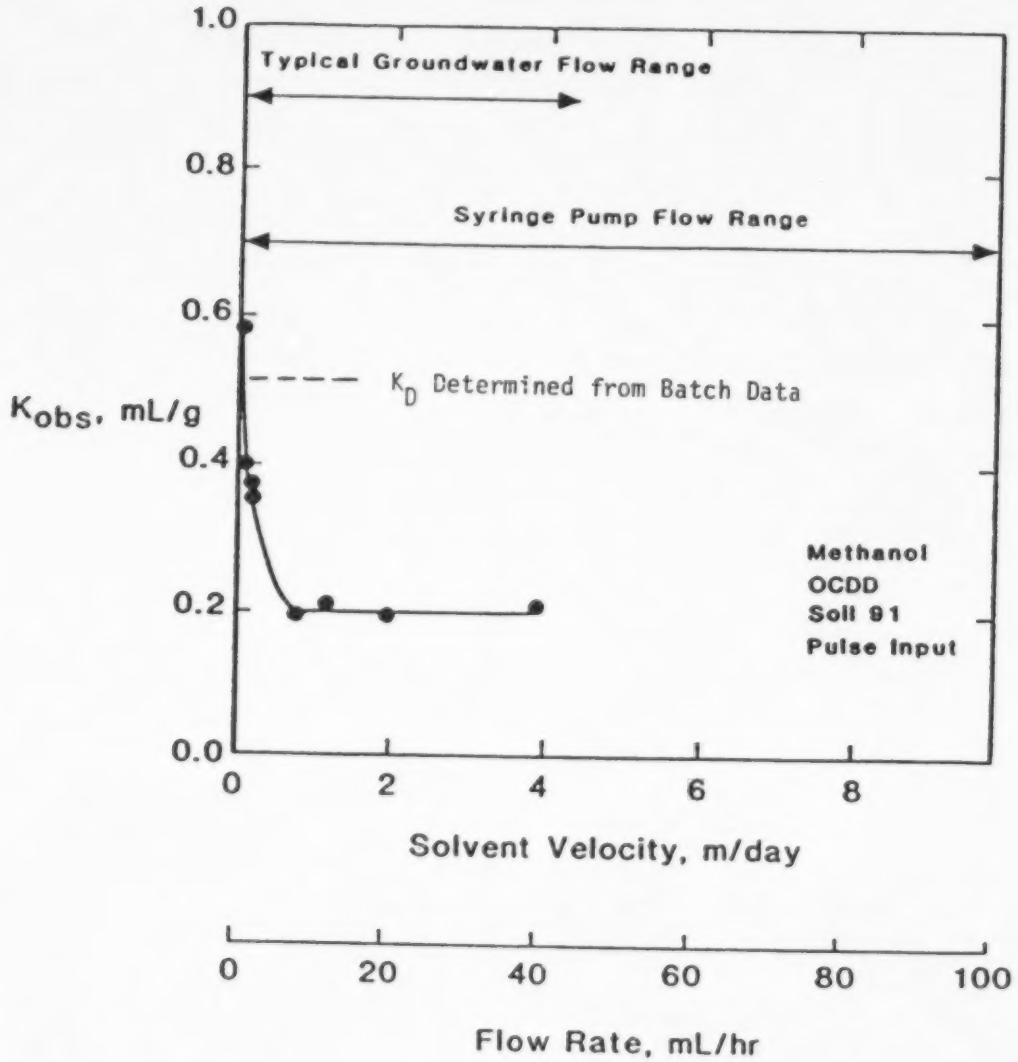

Figure 15. Plot of K_{obs} Versus Flow Rate for Sorptive Transport of O_8CDD Through Soil 91 at f_s of 1.0.

Batch experiments were conducted to generate sorption isotherm data for O_8CDD and both soils. The liquid phase in these experiments was f_s of 0.5 with PCP concentrations of 25 and 200 mg/L. Contact periods of 2 and 36 days were utilized for soils 91 and 96, respectively.

The results of the batch experiments are shown in Figures 16 and 17. For both soils and at both PCP concentrations, the sorption of O_8CDD in the presence of PCP was roughly 30% of the sorption of O_8CDD in the absence of PCP.

Column experiments were conducted for P_5CDD, H_6CDD and H_7CDD using soil 91. All experiments were conducted by injecting a 0.1-0.2 ug mass of the PCDD and by using a column flow rate of 8 mL/hr. Three liquid phases were used: f_s of 0.75; f_s of 0.75 and a PCP concentration of 1000 mg/L (which corresponds to 2.6% of PCP solubility at this f_s); and f_s of 0.75 and a CB concentration of 10 mL/L. The results of these experiments are summarized in Figure 18, which shows in histogram form K_{obs} for the three PCDDs in solvent, solvent with PCP and solvent with CB. For each PCDD studied, the lowest K_{obs} values were observed for the solvent/CB system, and K_{obs} for both solvent/CB and solvent/PCP systems were consistently below K_{obs} for solvent only. Values of K_{obs} in the presence of PCP and CB normalized to K_{obs} for systems containing water/methanol only are listed in Table 14. These normalized values show that PCDD sorption generally decreased by roughly 25% in the presence of PCP and roughly 50% in the presence of CB.

Column experiments were also conducted for all PCDDs at f_s of 0.9 with no PCP present and with PCP present at 1330 mg/L (which corresponds to roughly 1% of solubility at this f_s). The results of these experiments are shown in histogram form in Figure 19. The results for all PCDDs indicate that there was generally no significant change in K_{obs} in the presence of PCP relative to values of K_{obs} in the absence of PCP at a value of f_s of 0.9.

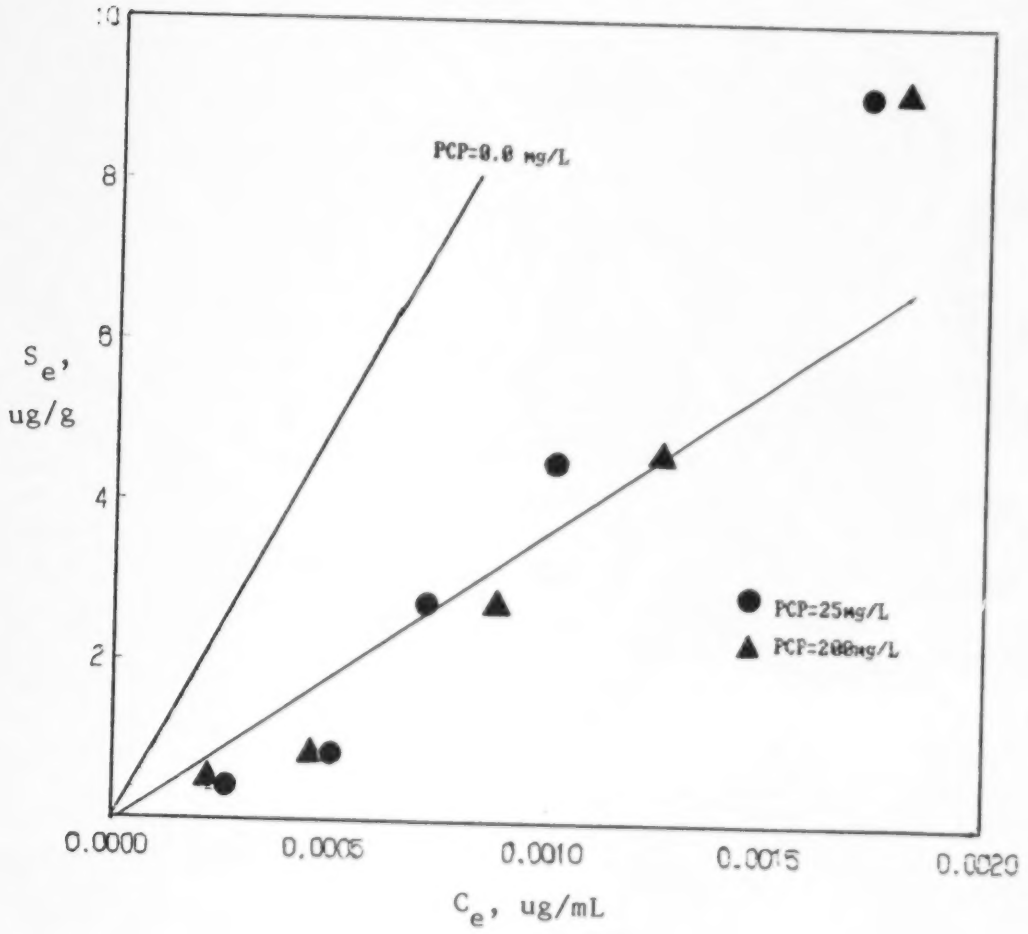

Figure 16. Plot of S_e Versus C_e for Sorption of O_8CDD by Soil 91 at f_s of 0.5.

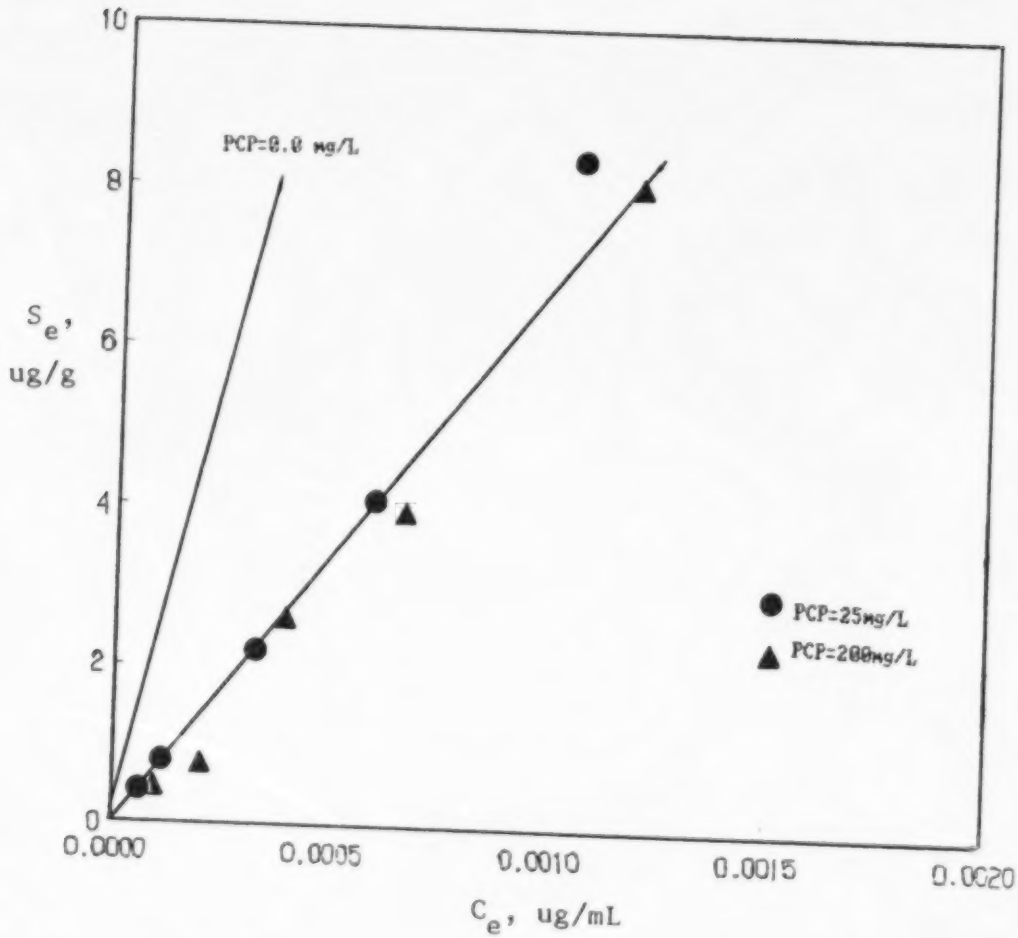

Figure 17. Plot of S_e Versus C_e for Sorption of O_8CDD by Soil 96 at f_s of 0.5.

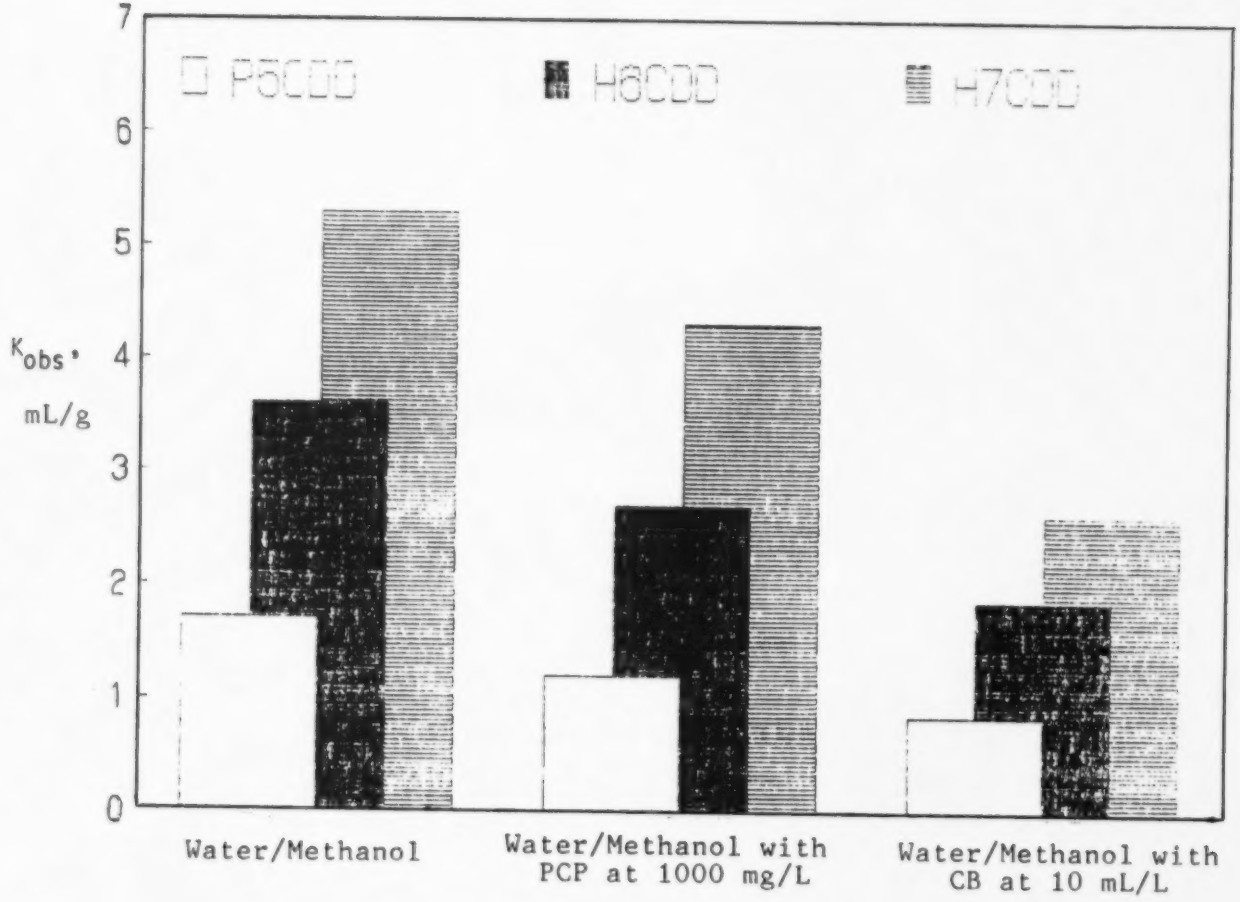

Figure 18. Histogram Showing Relative Variation in K_{obs} for Sorption of P_5CDD, H_6CDD and H_7CDD at f_s of 0.75 in the Presence of PCP and CB.

Table 14. Summary of the Reduction in K_{obs} Determined for Sorption of P_5CDD, H_6CDD and H_7CDD by Soil 91 at f_s of 0.75 in the presence of PCP and CB.

	$\frac{\text{Kobs with CB}}{\text{Kobs without CB}}$	$\frac{\text{Kobs with PCP}}{\text{Kobs without PCP}}$
P_5CDD	0.49	0.71
H_6CDD	0.52	0.75
H_7CDD	0.49	0.81

Figure 19. Histogram Showing Relative Variation in K_{obs} for Sorption of T_4CDD, P_5CDD, H_6CDD, H_7CDD and O_8CDD at f_s of 0.9 in the Presence of PCP.

The results of all experiments to evaluate the sorption of PCDDs in the presence of PCP are summarized in Figure 20. These results show that the effect of the presence of PCP was negligible at values of f_s of 0.9 but was more pronounced at lower f_s.

In theory, the reduced sorption of PCDDs in the presence of cosolutes demonstrated in the data presented in Figures 16-20 may be explained by a number of factors, including the effect of cosolute on the solubility of PCDDs (i.e., by affecting the liquid-phase activity coefficient of the PCDD) and/or the effect of cosolute on PCDD-soil organic matter interactions. On the basis of solubility effects documented for miscible cosolvents (Munz and Roberts, 1986; Fu and Luthy, 1986a; Yalkowsky and Roseman, 1981), it is not expected that PCDD solubility would be significantly influenced at such low cosolute concentrations (i.e., less than 1% by mass). However, this speculation has not yet been experimentally verified for cosolutes (either liquid or solid) of limited water solubility. Rather, it is suspected that the reduced sorption of PCDDs in the presence of the cosolutes may be explained in terms of either the effect of soil-phase cosolute on the soil-phase activity coefficients of the PCDDs or to competition between the sorbed cosolutes and PCDDs. This speculation would support the observation that the effects become more pronounced at lower f_s, because greater soil-phase concentrations of the cosolutes (either PCP or CB) would be expected via sorption as f_s decreases.

Mobility of Diesel Fuel

Screening studies involving batch and column experiments were conducted to assess the feasibility of conducting PCDD sorption experiments in the presence of diesel fuel. It was anticipated that experiments involving diesel fuel, which is immiscible in both water and water/methanol mixtures, might be complicated due to the presence and/or formation of multiple liquid-phases. These experiments were conducted without PCDDs to

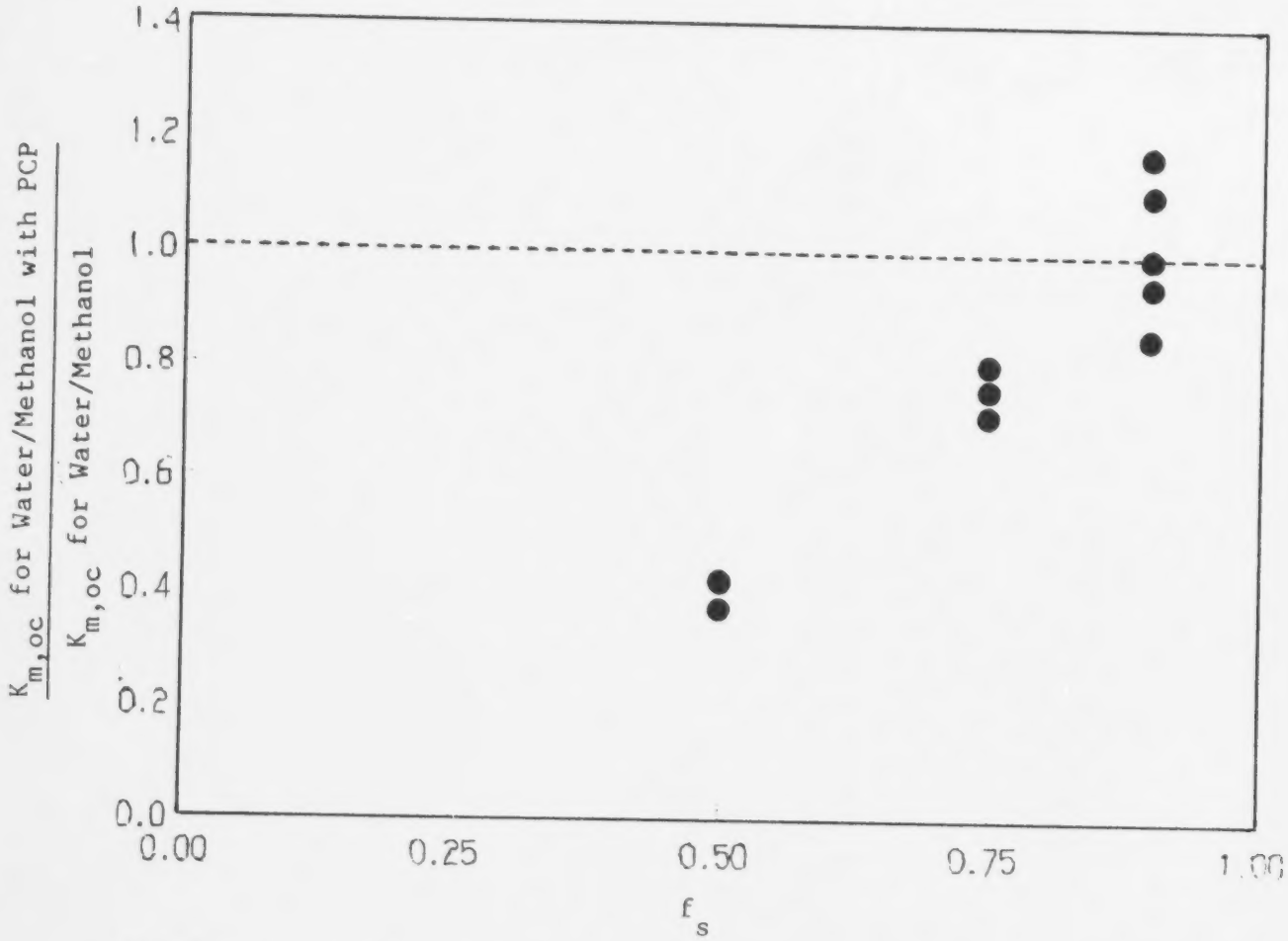

Figure 20. Ratio of $K_{m,oc}$ With PCP to $K_{m,oc}$ Without PCP Versus Volume Fraction Methanol for Sorption of PCDDs.

enable a qualitative evaluation of potential phase-formation problems.

Batch experiments were conducted by using 0.3 g of soil 91 coated with 100 uL of diesel fuel. This amount of diesel fuel was found to be sufficient to uniformly coat the soil. The soil was added to a centrifuge tube containing 12 mL of liquid phase (f_s of 0.5 and 0.75), and the mixture was contacted for 24 hours according to the batch shake test procedure described in Section 6. After contacting, the tubes were centrifuged for various times at 3,000 rpm. After centrifuging for as long as one hour, five or more phases were generally present in the mixture. A qualitative description of these phases is provided in Figure 21, which shows that diesel fuel had a significant effect on the integrity of the soil, having dispersed what appeared to be a major portion of the clay content and having contributed to the formation of a fairly stable suspension consisting presumably of liquid phase (water/methanol), diesel fuel and clay particles. These experiments indicated that batch experiments would not be feasible for conducting PCDD sorption experiments in the presence of diesel fuel, even at relatively high f_s. More importantly, however, the results of these experiments suggest the potential importance of the formation of multiple phases in the presence of diesel fuel. The potential for the formation of these phases under saturated-flow conditions was further investigated using soil column techniques.

Soil column experiments were conducted using soil 91 precoated with diesel fuel and a liquid phase at f_s of 0.75. The column contained 2 g of soil and roughly one-mL of diesel fuel. Initially, the column was eluted at a flow rate of 8 mL/hr during which one 16-mL effluent sample was collected. The flow rate was then reduced to 0.8 mL/hr and a second 16-mL effluent sample was collected. These samples were followed by collection of a third effluent sample of 16-mL collected at 8 mL/hr. Each of the effluent samples had unexpectely low turbidities (all below 40 NTU), suggesting that only a small portion of the diesel fuel had

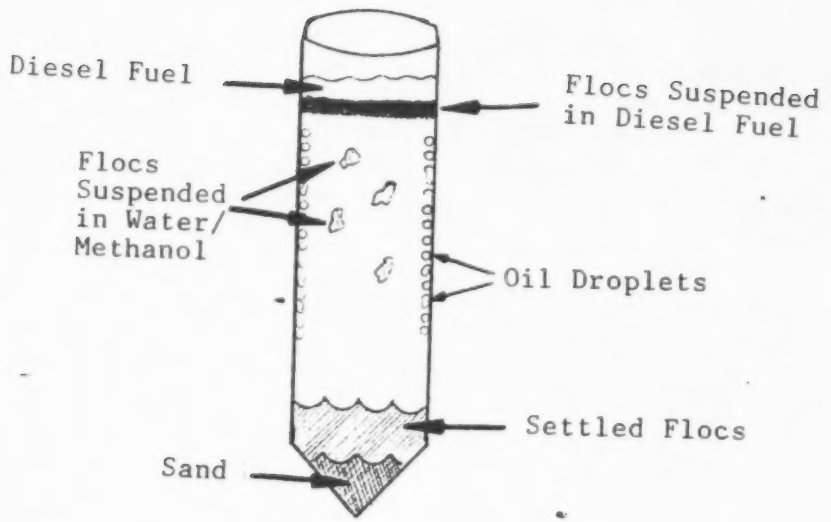

Figure 21. Representation of Phases Present Following Batch Experiments Involving Soil 91 and Diesel Fuel.

been leached from the column. Liquid-phase flow rate was then reduced to 0.16 mL/hr and the column was eluted for 100 hours. The effluent from the column during this period was collected as a fourth 16-mL effluent sample, and the results of turbidity analysis of this and the other three samples are shown in Figure 22. Under these conditions, the column effluent was a highly turbid, stable emulsion. From Figure 1, it was estimated that only 0.1-0.2 mL of diesel fuel had been eluted from the column.

The observations made from the soil column experiment involving diesel fuel (viz., that only about 20% of the diesel fuel was leached from the column and that more diesel fuel appeared to be leached at the lower flow rates) are not presently understood. The observations should be considered preliminary, particularly because they were made on the basis of a qualitative turbidity analysis of effluent samples. Caution in terms of evaluating these results is further warranted on the basis of the complexity of the mixture obtained by batch experiments shown in Figure 21. Nevertheless, plausible explanations for each of the observations can be made. It is suspected that the low apparent recovery of diesel fuel in these experiments may be related to the phenomena of residual saturation (Wilson and Conrad, 1984). Residual saturation refers to the retention of liquid within the voids of a soil, and liquid volumes as high as 40% of the void volume of the soil have been observed. The difference in effluent turbidity as a function of flow rate may reflect differences in the retention characterisitics of the soil column owing to such factors as kinetic and/or steric effects which limit the accessibility of the soil voids and/or pores. Turbidity characteristics may be influenced by these factors as well as others, such as the degree of dispersion of the liquid phase in water, the variability in components leached from the diesel fuel as it is aged via leaching, and the presence in the liquid/water mixture of organic matter from the parent soil.

Based on these observations, it can be concluded that stable emulsions may be formed as a result of soil-diesel fuel contact,

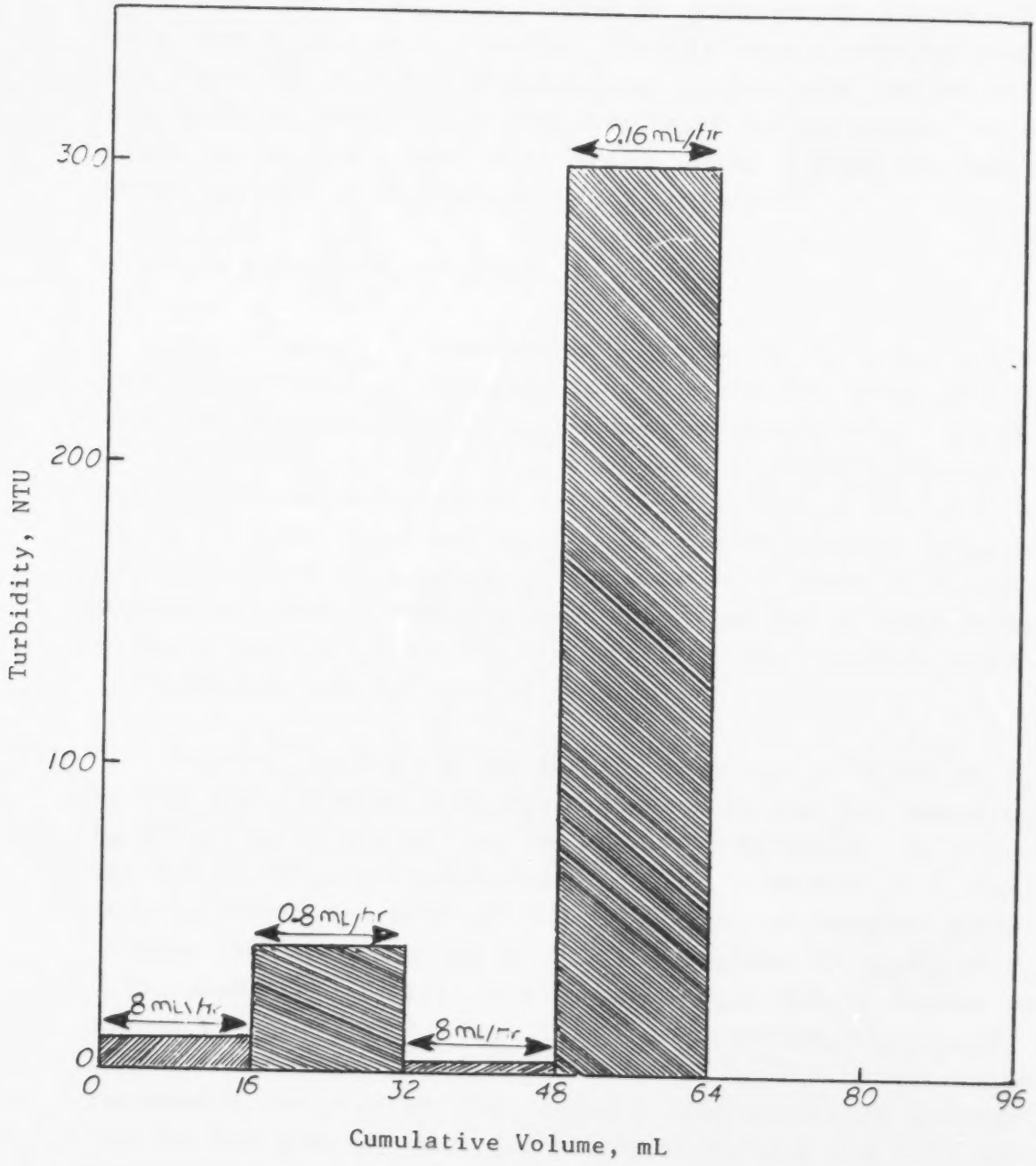

Figure 22. Plot of Effluent Turbidity Versus Cumulative Effluent Volume for Column Experiment Involving Soil 91 and Diesel Fuel at f_s of 0.75.

that diesel fuel may significantly affect the integrity of the soil, and that these effects can be achieved at environmentally realistic flow rates. Further work is recommended to evaluate the issue of emulsion formation as it pertains to contaminant transport in general and PCDD transport in particular at waste sites containing diesel fuel and/or other codisposed materials which may lead to the generation of emulsions.

SORPTION BY AQUIFER MATERIALS

The results of time-series experiments conducted by using batch techniques to evaluate the kinetics for sorption of the PCDDs by aquifer materials are plotted in Figures 23 and 24. For P_5CDD at f_s of 0.25, the data suggest that sorption equilibrium was attained at contact periods of 20 hr. For O_8CDD at f_s of 0.65, sorption equilibrium was attained in roughly 40 hr. For both solutes, sorption to the aquifer material was generally rapid. Based on the results of these experiments, a contact period of 48 hr was utilized to generate sorption isotherm data for the aquifer materials.

Typical isotherm plots for the sorption of P_5CDD at f_s of 0.4 by the Traverse City aquifer material and for sorption of O_8CDD at f_s of 0.8 by the Lula aquifer material are shown in Figures 25 and 26, respectively. Linear isotherms were observed for all PCDDs for both of the f_s values and aquifer materials studied with the exception of T_4CDD and O_8CDD. For T_4CDD at f_s of 0.25, isotherm linearity was observed only for C_e values below 0.0005 ug/mL. For O_8CDD at f_s of 0.65, isotherm linearity was observed only for C_e values below 0.005 ug/mL. The results of regression analysis of the isotherm data according to equation (2) for the data obtained for the Traverse City and Lula aquifer materials are summarized in Tables 15 and 16, respectively. Included in Tables 15 and 16 are the experimental value of K_{Di}, as well as values of liquid phase V_{mi}, $K_{m,oc}$ and $\log(K_{m,oc})$.

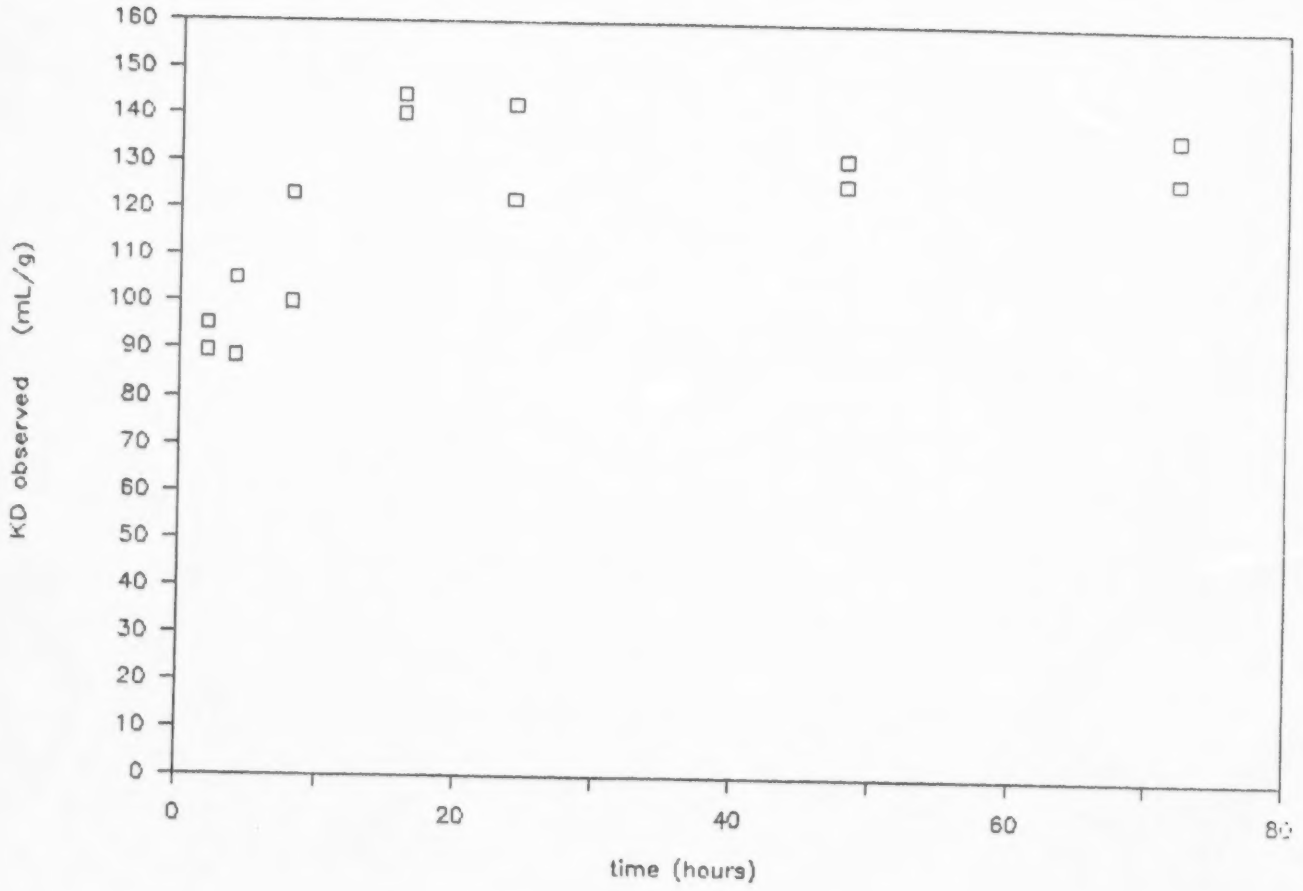

Figure 23. Plot of K_D Versus Contact Time for Sorption of P_5CDD at f_s of 0.25 by Traverse City Aquifer Material.

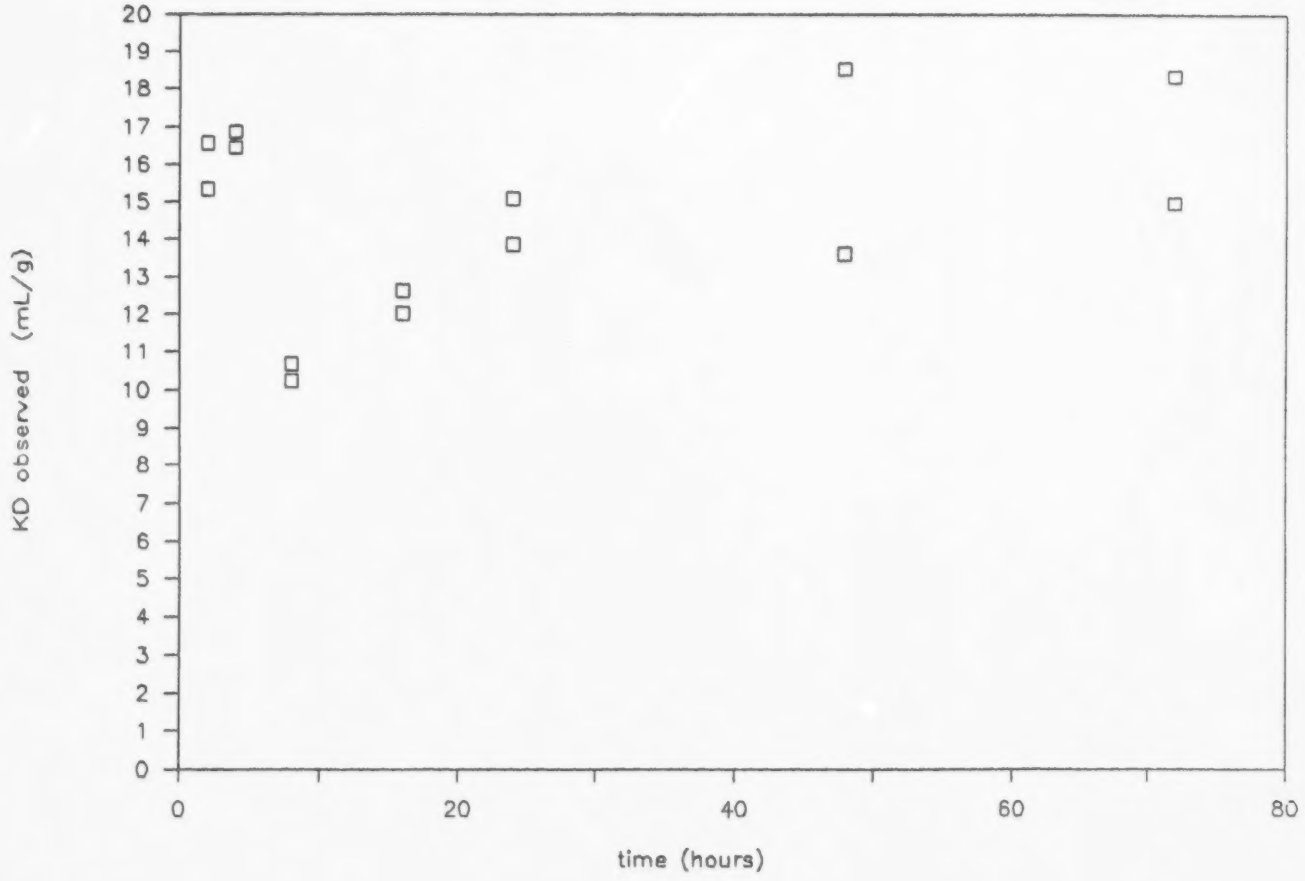

Figure 24. Plot of K_D Versus Contact Time for Sorption of O_8CDD at f_s of 0.65 by Traverse City Aquifer Material.

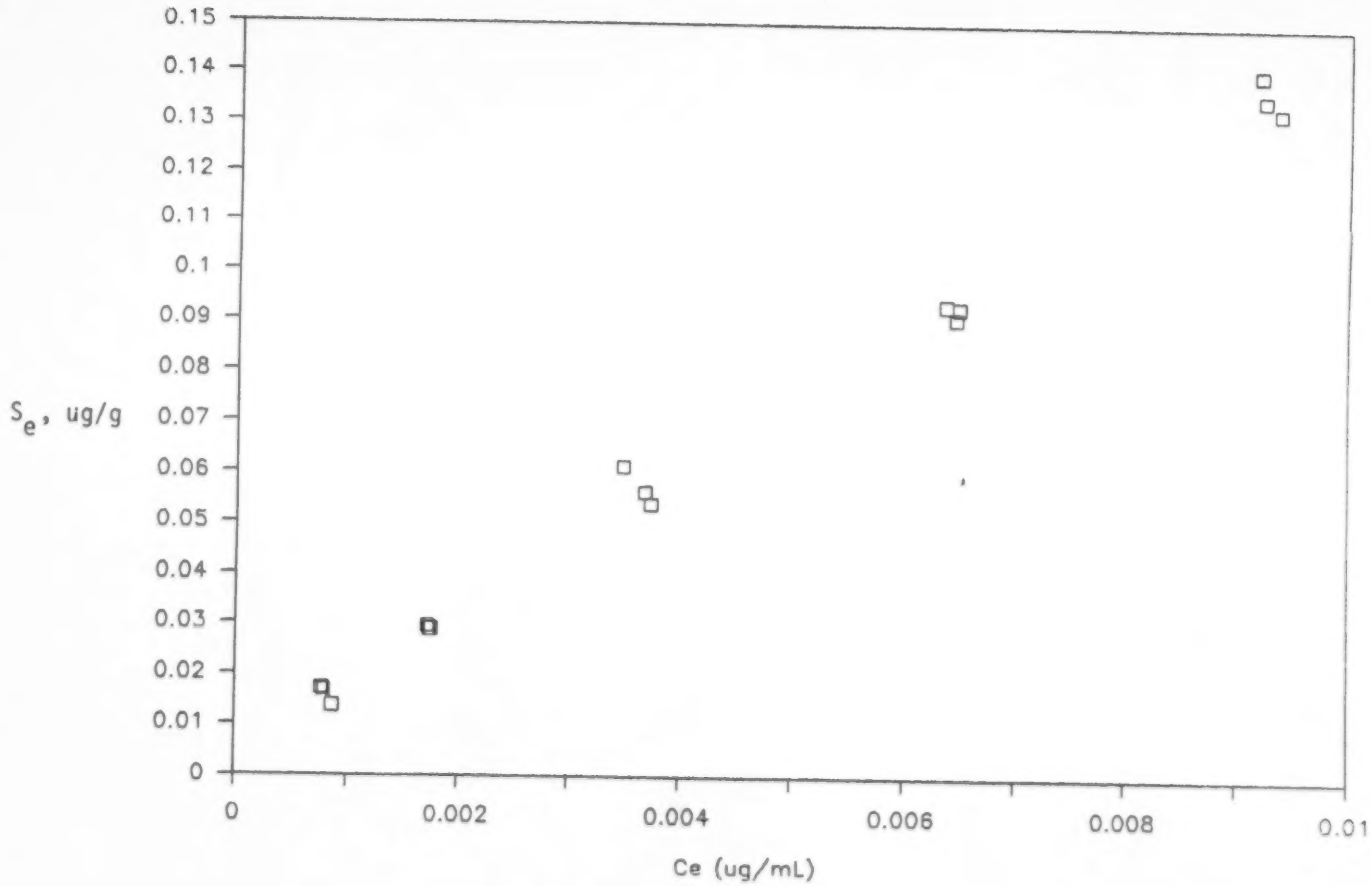

Figure 25. Plot of S_e Versus C_e for Sorption of P_5CDD by Traverse City Aquifer Material at f_s of 0.4.

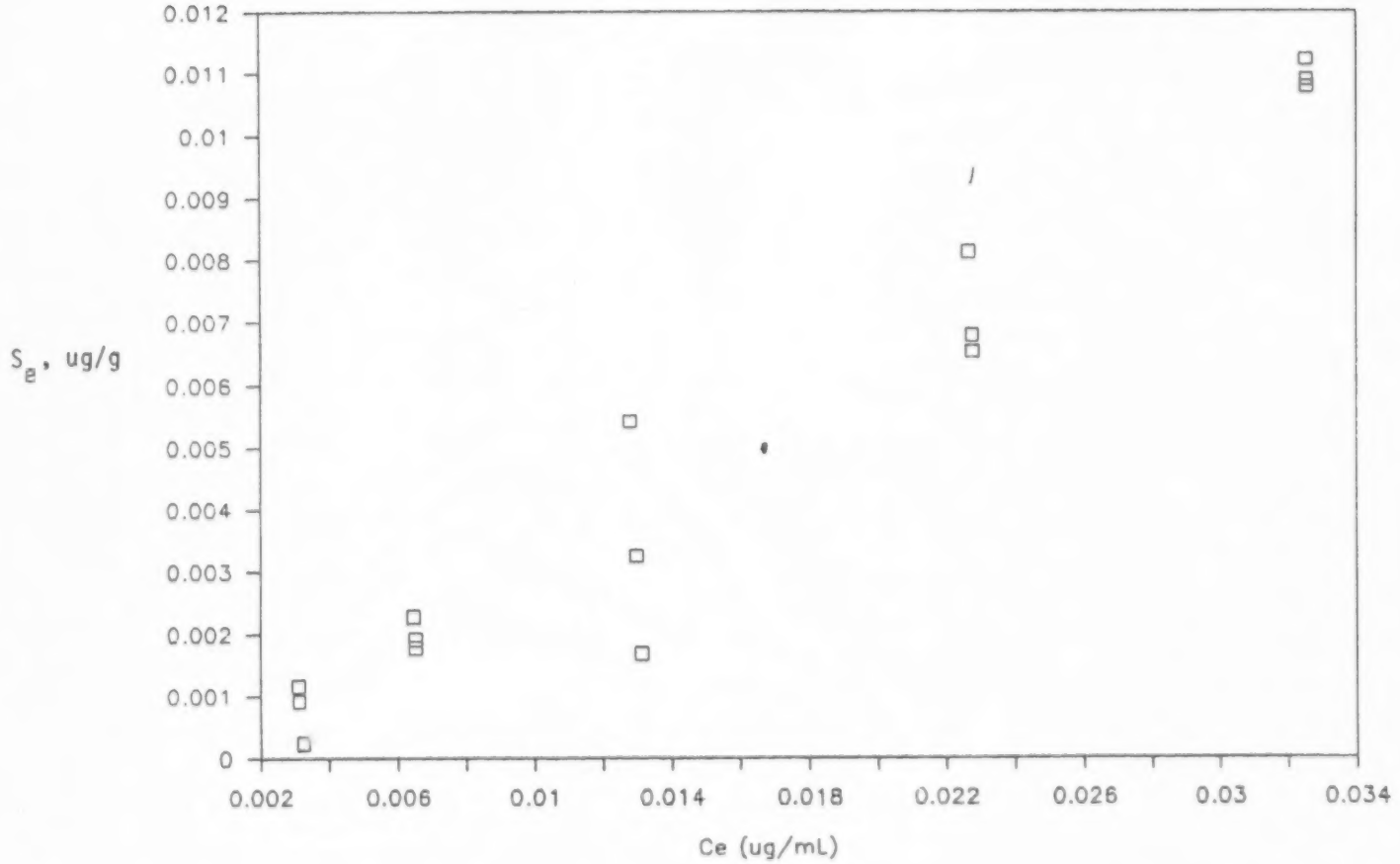

Figure 26. Plot of S_e Versus C_e for Sorption of O_8CDD by Lula Aquifer Material at f_s of 0.8.

Table 15. Summary of Isotherm Parameters Determined for Sorption of T_4CDD, P_5CDD, H_6CDD, H_7CDD and O_8CDD by Traverse City Aquifer Material from Water/Methanol Mixtures.

PCDD	f_s	K_D, mL/g	n	r^2	V_m, mL/mol	$K_{m,oc}$, mol/g	$\log(K_{m,oc})$
T_4CDD	0.25	63	6	0.99	20.5	18,000	4.3
	0.4	16	15	0.96	22.4	4,100	3.6
P_5CDD	0.3	72	15	0.98	21.1	20,000	4.3
	0.4	15	15	1.00	22.4	3,900	3.6
H_6CDD	0.5	7.9	15	0.99	24.1	1,900	3.3
	0.65	1.6	15	0.97	27.1	350	2.5
H_7CDD	0.5	13	15	0.97	24.1	3,200	3.5
	0.65	1.8	15	0.92	27.1	390	2.6
O_8CDD	0.65	5.1	12	0.89	27.1	1,100	3.0
	0.8	0.7	15	0.94	31.5	130	2.1

Table 16. Summary of Isotherm Parameters Determined for Sorption of T_4CDD, P_5CDD, H_6CDD, H_7CDD and O_8CDD by Lula Aquifer Material from Water/Methanol Mixtures.

PCDD	f_s	K_D, mL/g	n	r^2	V_m, mL/mol	$K_{m,oc}$, mol/g	$\log(K_{m,oc})$
T_4CDD	0.25	60	6	0.95	20.5	14,000	4.1
	0.4	7.3	15	1.00	22.4	1,600	3.2
P_5CDD	0.3	33	15	0.99	21.1	7,400	3.9
	0.4	7.7	15	1.00	22.4	1,600	3.2
H_6CDD	0.5	6.0	15	0.99	24.1	1,200	3.1
	0.65	1.5	15	0.95	27.1	270	2.4
H_7CDD	0.5	11	15	0.94	24.1	2,300	3.4
	0.65	1.5	15	0.99	27.1	270	2.4
O_8CDD	0.65	6.3	12	0.86	27.1	1,100	3.0
	0.8	0.3	15	0.98	31.5	49	1.7

Values of $\log(K_{m,oc})$ in Tables 15 and 16 for each of the PCDDs are plotted versus f_s in Figures 27-31. The values of $\log(K_{m,oc})$ determined by Guiseppi-Elie (1987) for each of the PCDDs using surface soils (soils 91 and 96) and the regression equations corresponding to these data are also plotted in Figures 27-31. Regression analyses were performed using equation (8) and the data for the aquifer materials and the combined data for the aquifer materials and surface soils, and the results of these analyses are summarized in Table 17. Comparison of the experimental data points for the aquifer materials with the data for the surface soils and the plotted regression equations indicates that values of $\log(K_{m,oc})$ for both sets of sorbents are well described by a single line for T_4CDD, H_6CDD and H_7CDD. For P_5CDD, the experimental values of $\log(K_{m,oc})$ for the aquifer materials at each f_s are significantly greater than those predicted based on the regression equation of the surface soils. For O_8CDD, the experimental values of $\log(K_{m,oc})$ for the aquifer materials are slightly below those predicted base on the regression equation of the surface soils.

It was initially anticipated that the values of $\log(K_{m,oc})$ determined for the aquifer materials might be greater than the corresponding values determined for the surface soils. This anticipation was based on the evidence in the literature which suggests that sorption of an organic solute to a sorbent with f_{oc} below about 0.001 is greater than would be expected based on the values of K_{OC} determined for the solute using sorbents with f_{oc} values above 0.001 (Schwarzenbach and Westall, 1981). It has been speculated that sorption to sorbents with low f_{oc} is comprised of contributions from solute-mineral interactions as well as solute-organic carbon interactions (Karickhoff, 1984; Curtis et al., 1986). The general agreement between values of $\log(K_{m,oc})$ for the aquifer materials and the surface soils for PCDDs suggests that f_{oc} alone is the dominant factor determining the extent of sorption for highly hydrophobic organic contaminants such as PCDDs, presumably because the sorption is sufficiently strong to dominate the weaker sorption to minerals.

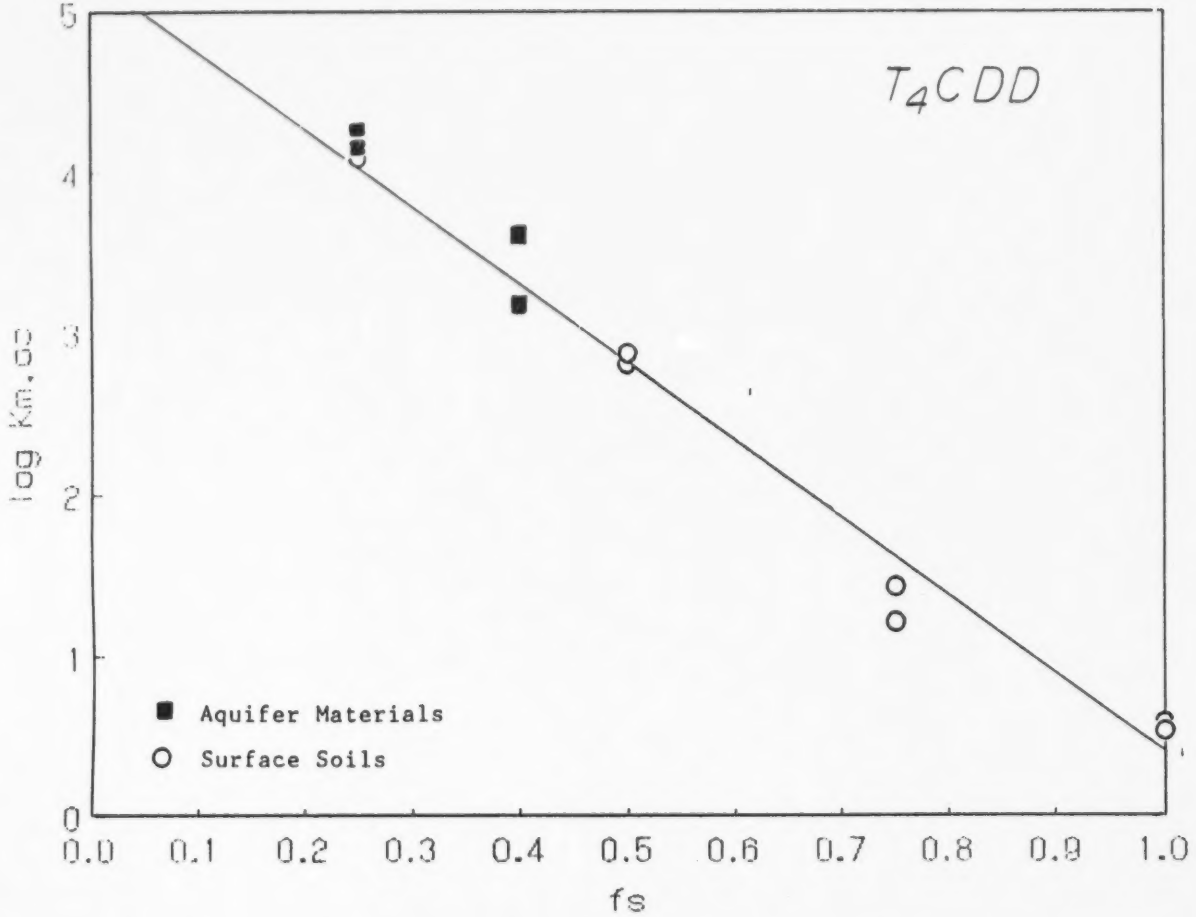

Figure 27. Log-Linear Plot of $K_{m,OC}$ Versus Volume Fraction Methanol for Sorption of T_4CDD by Lula and Traverse City Aquifer Materials.

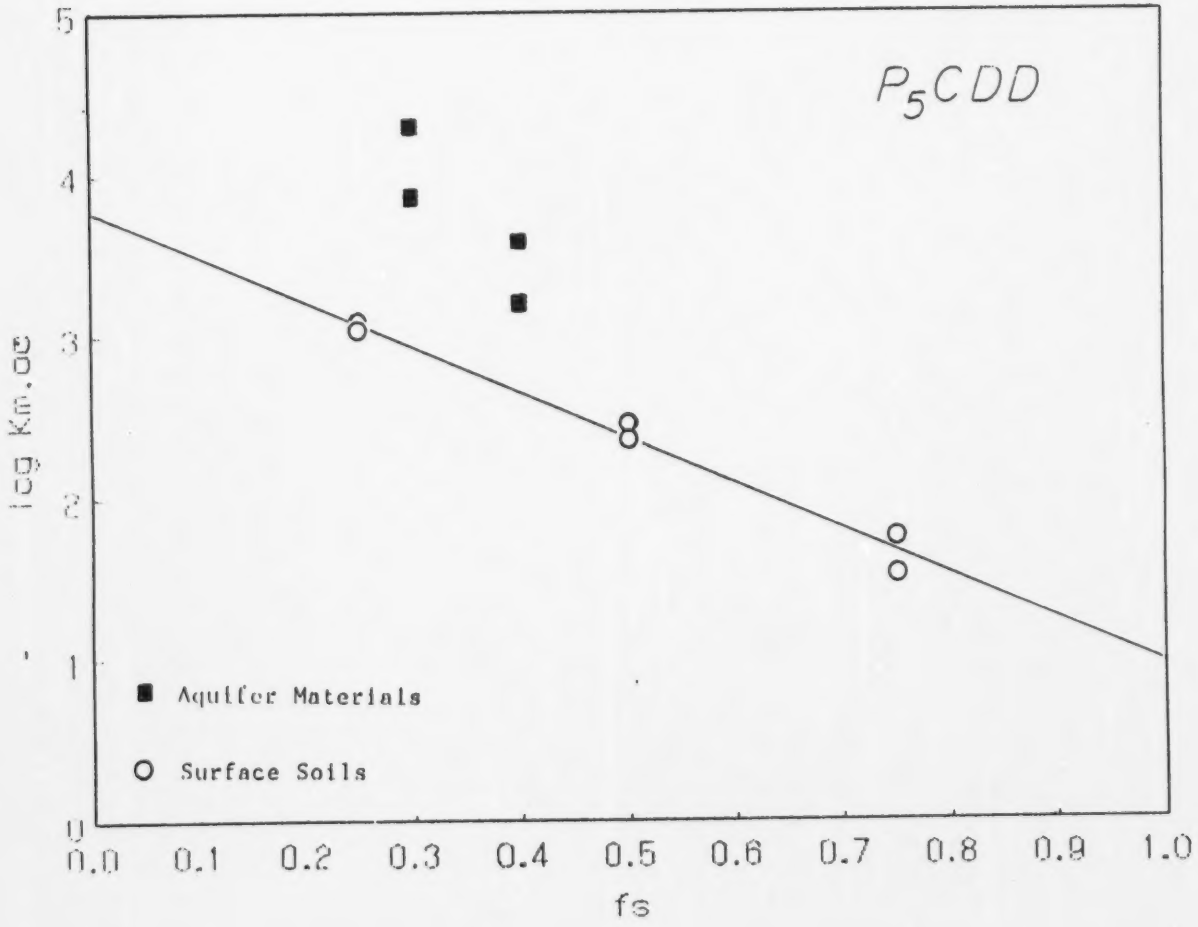

Figure 28. Log-Linear Plot of $K_{m,oc}$ Versus Volume Fraction Methanol for Sorption of P_5CDD by Lula and Traverse City Aquifer Materials.

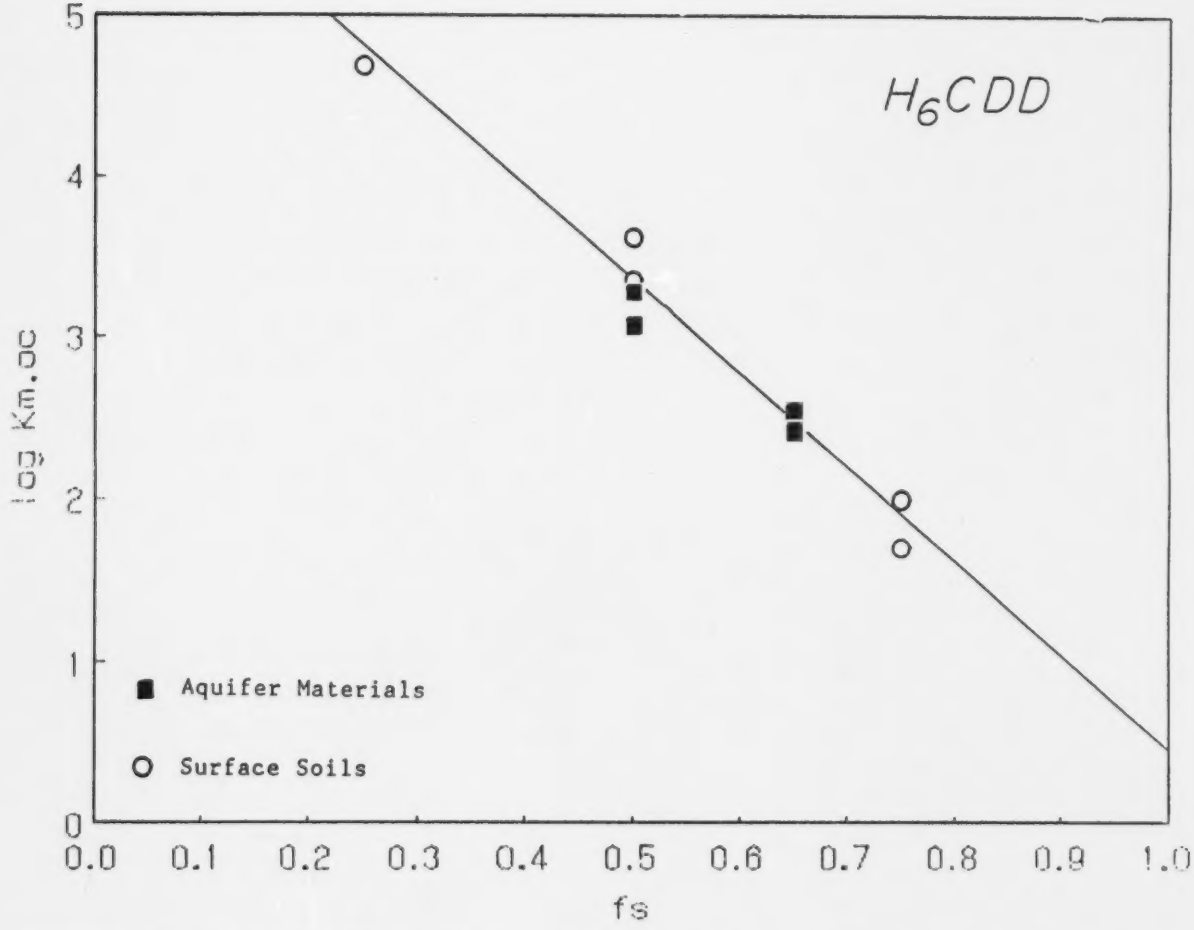

Figure 29. Log-Linear Plot of $K_{m,oc}$ Versus Volume Fraction Methanol for Sorption of H_6CDD by Lula and Traverse City Aquifer Materials.

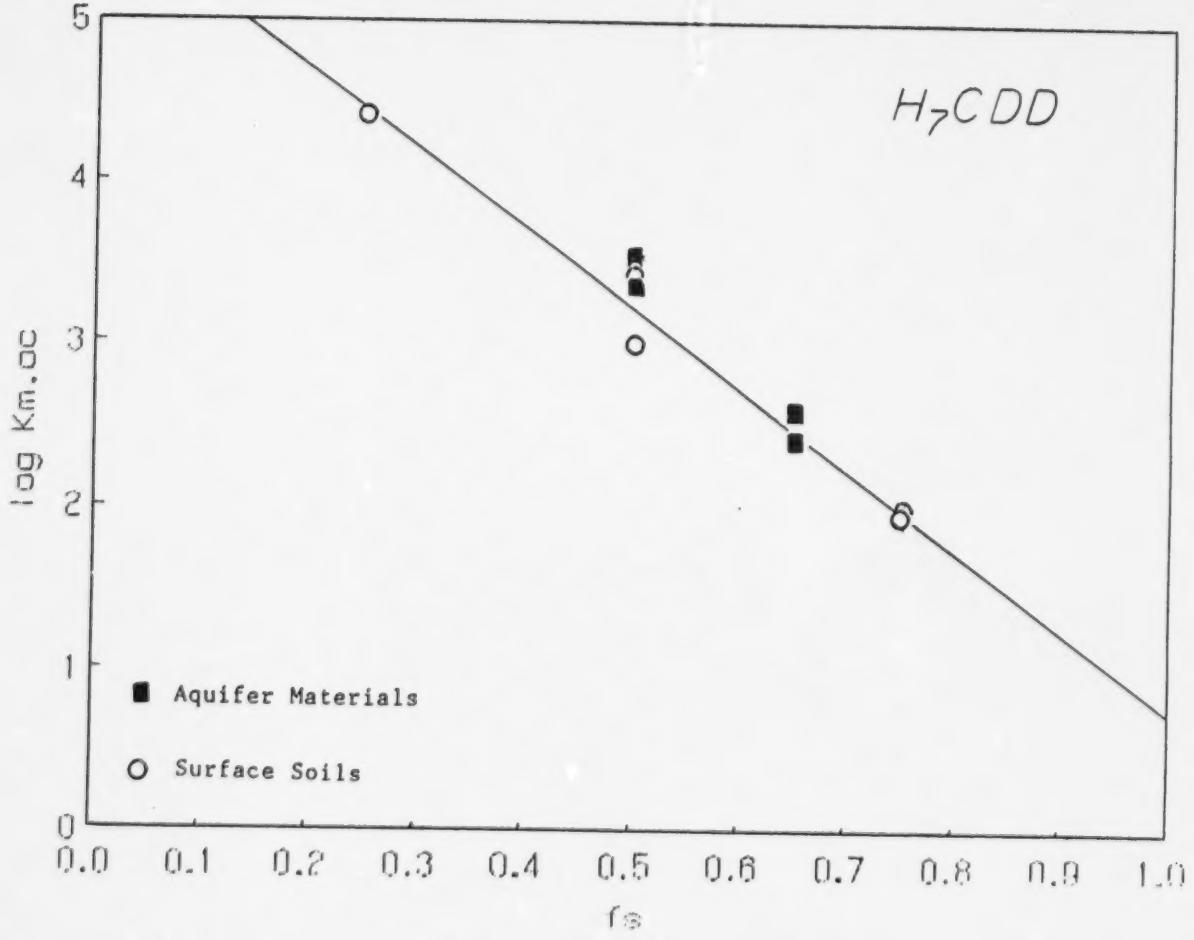

Figure 30. Log-Linear Plot of $K_{m,oc}$ Versus Volume Fraction Methanol for Sorption of H_7CDD by Lula and Traverse City Aquifer Materials.

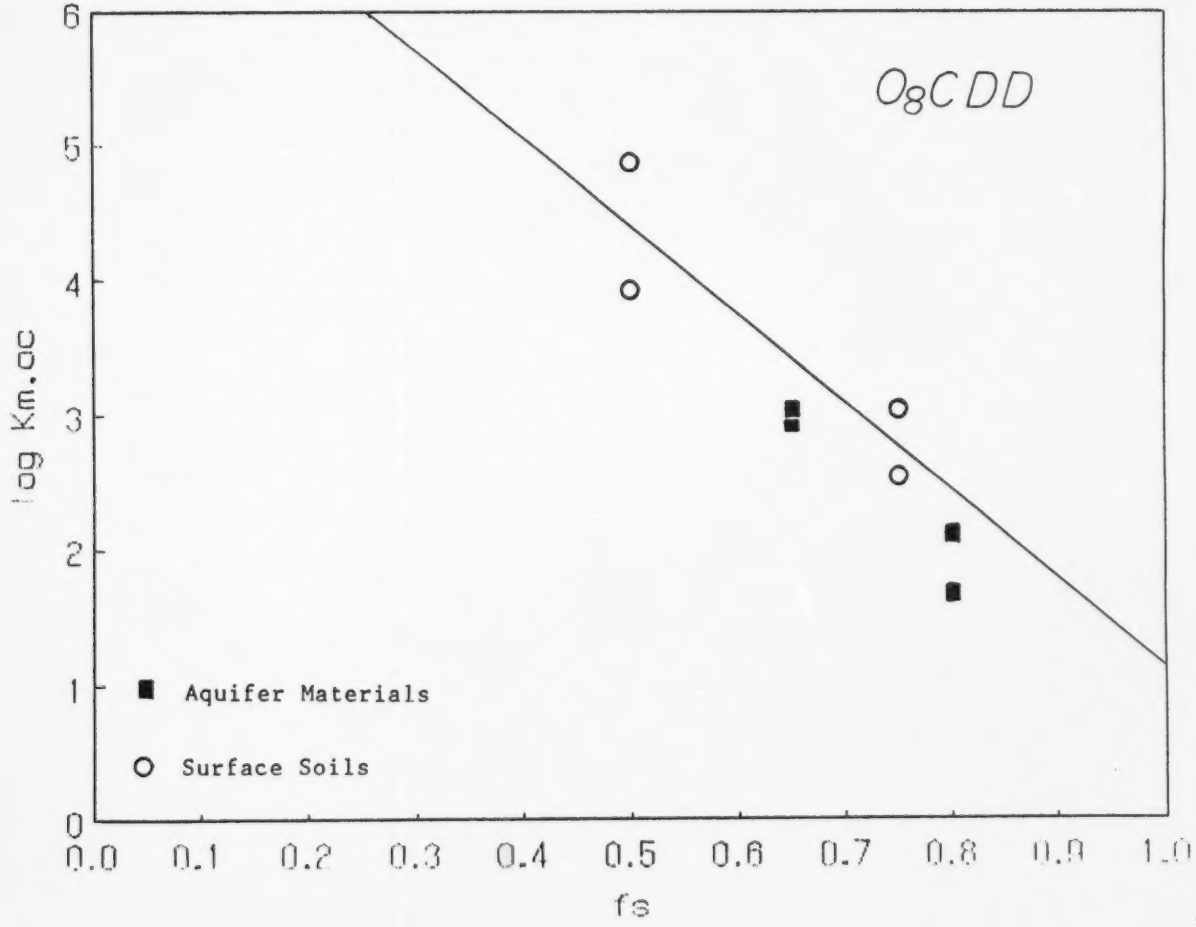

Figure 31. Log-Linear Plot of $K_{m,oc}$ Versus Volume Fraction Methanol for Sorption of O_8CDD by Lula and Traverse City Aquifer Materials.

Table 17. Summary of Cosolvent Theory Regression Parameters Determined for Sorption of T_4CDD, P_5CDD, H_6CDD, H_7CDD and O_8CDD by Aquifer Materials from Water/Methanol Mixtures.

	Aquifer Materials	Surface Soils	Combined Data
T_4CDD			
$\alpha\sigma_s$	5.33	4.83	5.00
$\log(K_{m,w,oc})$	5.53	5.23	5.37
r^2	0.87	0.98	0.98
P_5CDD			
$\alpha\sigma_s$	6.87	2.83	4.05
$\log(K_{m,w,oc})$	6.15	3.79	4.70
r^2	0.74	0.98	0.71
H_6CDD			
$\alpha\sigma_s$	4.64	5.81	5.71
$\log(K_{m,w,oc})$	5.50	6.28	6.17
r^2	0.94	0.98	0.97
H_7CDD			
$\alpha\sigma_s$	6.09	4.90	5.00
$\log(K_{m,w,oc})$	6.48	5.66	5.77
r^2	0.97	0.97	0.96
O_8CDD			
$\alpha\sigma_s$	7.63	6.45	7.62
$\log(K_{m,w,oc})$	8.01	7.63	8.18
r^2	0.94	0.82	0.86

The high $K_{m,oc}$ values determined for P_5CDD and the aquifer materials relative to $K_{m,oc}$ values determined for surface soils differs from the general behavior of the other PCDDs studied. The apparent anomalous behavior of P_5CDD is not presently understood. However, Guiseppi-Elie (1987) has noted other anomalies in the behavior of P_5CDD, including the relatively low sorption by surface soils from water/methanol mixtures and the relatively high solubilities in water and methanol. Although sorption would be expected to increase and solubility to decrease as the number of chlorine atoms in the PCDD molecules increases in the series from T_4CDD through O_8CDD, the actual sorptive and solubility behavior of P_5CDD places it before T_4CDD in this series. Guiseppi-Elie (1987) has speculated that the anomalous behavior of P_5CDD may result from the nonsymmetrical positions of the chlorine atoms (located at the 1, 2, 3, 4 and 7 positions) relative to the more symmetrical distribution of the chlorine atoms within the molecules of the other PCDDs. It is possible that the chlorine asymmetry of P_5CDD may result in stronger mineral interactions (as well as weaker organic carbon interactions), and may explain the relative differences observed for sorption of P_5CDD by surface soils and aquifer materials. Sorption and solubility studies involving other P_5CDD isomers need to be conducted to better understand this phenomena.

DESORPTION FROM SURFACE SOILS

The data generated by time series experiments to evaluate the kinetics of desorption of PCDDs from surface soils are summarized in Table 18. The information in Table 18 includes, for each of the four PCDDs and two surface soils studied, the individual-point K_D values determined for the initial sorption of the PCDDs to the soils for the thirty-day contact periods, and the desorption partition ratio K_{des}. Both K_D and K_{des} were determined on the basis of measured liquid-phase PCDD concentrations and soil-phase concentrations determined by mass balance (i.e., soil-phase PCDD concentrations were not directly

Table 18. Summary of Results for Desorption Time Series Experiments for Soils 91 and 96 and All PCDDs.

	T_4CDD	P_5CDD	H_6CDD	H_7CDD	O_8CDD
Soil 91					
K_D, mL/g	6±1	5±2	7±1	10±3	30±3
n	10	9	10	10	10
t, days; K_{des}, mL/g	1; 67	2; 69	1; 28	1; 30	1; 150
	5; 56	5; 41	6; 19	5; 18	5; 152
	13; 43	9; 27	10; 13	10; 50	11; 110
	34; 44	38; 27	22; 17	20; 12	21; 84
			43; 12	46; 30	30; 110
Soil 96					
K_D, mL/g	120±6	140±10	240±32	190±8	520±45
n	10	10	10	10	10
t, days; K_{des}, mL/g	1; 480	2; 250	1; 1500	1; 910	1; 1800
	5; 300	5; 200	6; 1100	5; 560	5; 1000
	13; 210	9; 170	10; 760	10; 540	10; 890
	34; 230	38; 170	22; 410	20; 300	20; 1000
			43; 500	46; 380	31; 650

measured). Values of K_{des} were determined at desorption contact periods ranging from 1-30 days.

The results of regression analysis of the data in Table 18 according to equations (14) and (15) are presented in Table 19. In general, it was found that the power curve model, with a value of b of roughly 0.5, provided a better fit to the data than did the exponential (i.e., first order) model. A time series plot of K_{des} for the data of H_6CDD and soil 96 and the power curve determined by regression of these data is shown in Figure 32. From Figure 32, it is apparent that a 43-day desorption contact period for H_6CDD was not sufficient to achieve complete reversible desorption of H_6CDD. However, for this system K_{des} values of 400-500 mL/g correspond to a fractional approach to reversible desorption (i.e., the actual mass of PCDD desorbed relative to the maximum mass that would be desorbed for complete reversibility according to the sorption K_D) of roughly 0.60. Values for the fractional approach to reversible desorption determined for all PCDDs and soils are summarized in Table 20.

From these limited data, it appeared that the desorption of PCDDs from the surface soils into water/methanol mixtures may be reversible, but that desorption is characterized by very low desorption rates. This observation is in agreement with that made by Guiseppi-Elie (1987) for desorption of T_4CDD from soils into water/methanol mixtures. Additional research is recommended to further investigate the desorption of PCDDs from soils into water/methanol mixtures, particularly at low f_s values which are typical of environmental conditions.

Table 19. Summary of Results Obtained by Regression Analysis of the Desorption Time Series Data for Soil 96 and the PCDDs.

			Exponential			Power Curve		
PCDD	K_D, mL/g	n	a	b	r^2	a	b	r^2
T_4CDD	120	10	220	-0.024	0.37	305	-0.34	0.66
P_5CDD	140	10	75	-0.044	0.31	160	-0.66	0.36
H_6CDD	260	10	840	-0.041	0.51	1500	-0.56	0.68
H_7CDD	190	10	440	-0.028	0.41	720	-0.44	0.69
O_8CDD	520	10	930	-0.061	0.67	1300	-0.55	0.68

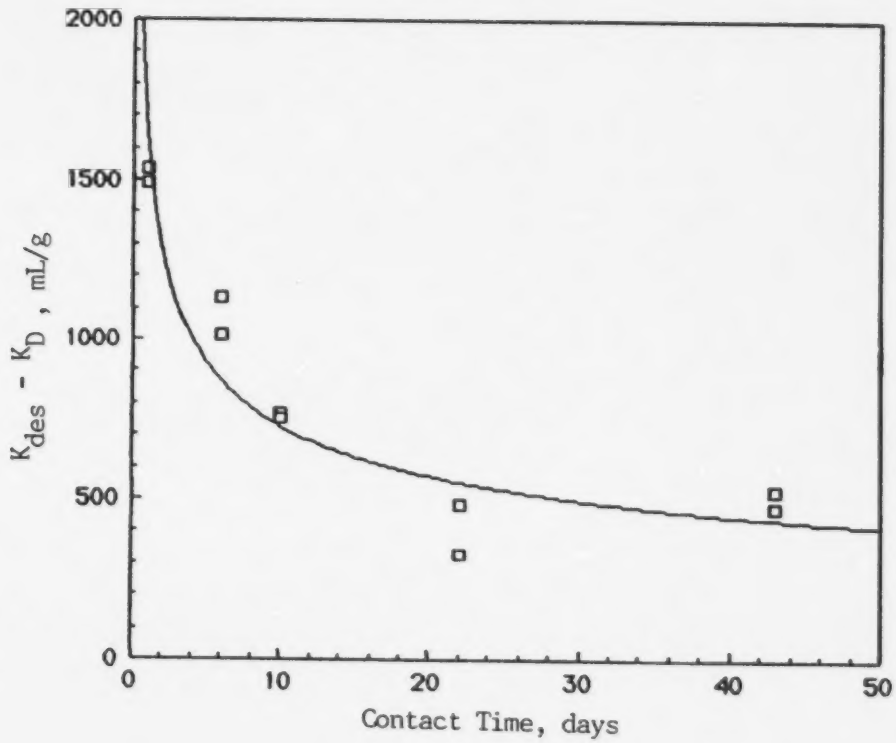

Figure 32. Time Series Plot of K_{des} for Desorption of H_6CDD from Soil 96 at f_s of 0.75.

Table 20. Fractional Approach to Reversible Desorption Determined for All PCDDs.

	Soil 91	Soil 96
T_4CDD	0.48	0.62
P_5CDD	0.70	0.85
H_6CDD	0.86	0.63
H_7CDD	0.78	0.64
O_8CDD	0.64	0.85

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